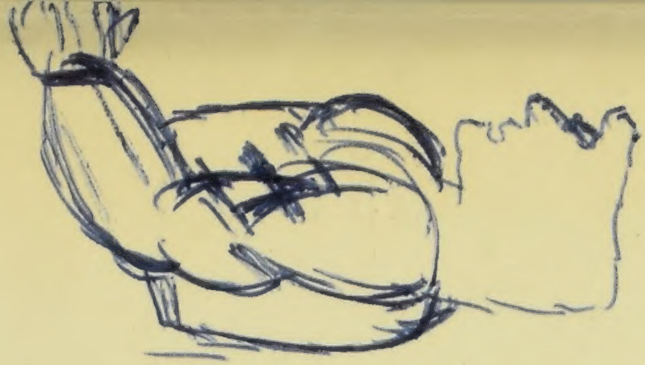
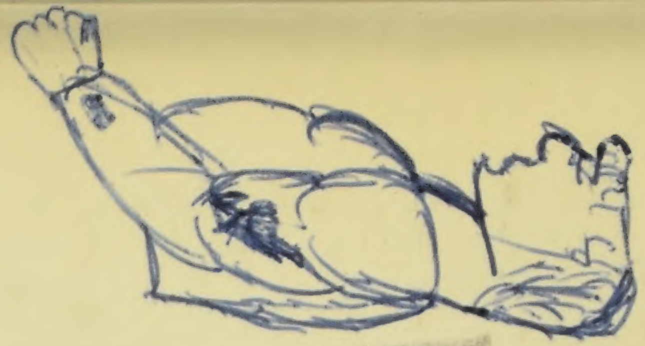
ELEMENTARY CHEMISTRY

GUEST

THE SYMBOLS, APPROXIMATE ATOMIC WEIGHTS AND VALENCES OF THE MORE IMPORTANT ELEMENTS

Element	*Symbol*	*Approx. At. Wt.*	*Valence*
Aluminum	Al	27	III
Antimony	Sb	122	III V
Arsenic	As	75	III V
Barium	Ba	137	II
Bismuth	Bi	209	III
Boron	B	11	III
Bromine	Br	80	I
Cadmium	Cd	112.4	II
Calcium	Ca	40	II
Carbon	C	12	IV
Chlorine	Cl	35.5	I
Chromium	Cr	52	II III VI
Cobalt	Co	59	II III
Copper	Cu	63.6	I II
Fluorine	F	19	I
Gold	Au	197	I III
Hydrogen	H	1	I
Iodine	I	127	I
Iron	Fe	56	II III
Lead	Pb	207	II IV
Lithium	Li	7	I
Magnesium	Mg	24	II
Manganese	Mn	55	II IV
Mercury	Hg	200	I II
Nickel	Ni	58.7	II
Nitrogen	N	14	III V
Oxygen	O	16	II
Phosphorus	P	31	III V
Platinum	Pt	195	II IV
Potassium	K	39	I
Radium	Ra	226	II
Silicon	Si	28	IV
Silver	Ag	108	I
Sodium	Na	23	I
Sulphur	S	32	II IV VI
Tin	Sn	119	II IV
Zinc	Zn	65	II





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BY

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SIR ISAAC PITMAN & SONS (CANADA), LTD.
381-3 CHURCH STREET TORONTO

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SIR ISAAC PITMAN & SONS (CANADA), LTD.
(INCORPORATING THE COMMERCIAL TEXT BOOK COMPANY)
PITMAN HOUSE, 381-383 CHURCH STREET, TORONTO
ASSOCIATED COMPANIES
SIR ISAAC PITMAN & SONS, LTD.
PITMAN HOUSE, PARKER STREET, KINGSWAY, LONDON, W.C. 2
THE PITMAN PRESS, BATH
PITMAN HOUSE, LITTLE COLLINS STREET, MELBOURNE
UNITEERS BUILDING, RIVER VALLEY ROAD, SINGAPORE
27 BECKETTS BUILDINGS, PRESIDENT STREET, JOHANNESBURG
PITMAN PUBLISHING CORPORATION
2 WEST 45TH STREET, NEW YORK
205 WEST MONROE STREET, CHICAGO

Printed and Bound by
The Hunter Rose Co. Limited, Toronto

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PREFACE

The writing of this book is the result of many years of experience in the teaching of chemistry in Canadian High Schools. It was written to meet the requirements of the Quebec High School leaving syllabus in chemistry. However, enough subject matter has been included to satisfy the requirements of the usual high school course in this subject.

Some of the important features of the text may be summarized as follows:

1. It is written for the student. This objective has determined the style of writing, the chapter arrangement, and the subject matter.
2. An attempt has been made to arrange the material in a logical manner.
3. The fundamental laws and theories have been explained in such a way as to make them readily understood by the student.
4. Special emphasis has been placed on the applications of chemistry to industry and to everyday life.
5. Descriptions and illustrations of industrial processes have been carefully considered in the light of the most recent developments.
6. A large number of tables and illustrations have been included in the book to make it more interesting and attractive to the student.
7. Review exercises are given at the end of each chapter.
8. To assist the student in reviewing for examinations a comprehensive collection of review questions and problems has been placed in the appendices.
9. For those schools which are equipped for showing moving pictures, a comprehensive list of available films on chemical topics is included in the appendices.
10. The text has been planned for use in conjunction with the laboratory manual, "Experiments in Elementary Chemistry," by the same author.

ACKNOWLEDGMENTS

The author wishes to acknowledge his indebtedness for suggestions which were most helpful in the writing of this book. He wishes especially to mention Mr. B. G. Spracklin, of the Baron Byng High School, Montreal, who very kindly criticized the manuscript.

It is also a pleasure to acknowledge the interest of Dr. F. F. Osborne, of McGill University, who supplied material for the geological background of Chapter 56; of Miss Margaret I. Garlick, of the High School for Girls, Montreal; of Miss Ann M. Munn, of the High School of Montreal; and of Mr. M. D. Atko and Mr. E. Assaly who were very helpful in the preparation of a number of the illustrations. Appreciation is extended to a number of industrial firms for their courtesy in furnishing illustrations.

Acknowledgment is also due to Mr. W. V. Waddoup, Chief Assistant Master, Dulwich Road Senior Boys' School, Birmingham, for permission to reproduce a number of illustrations from his book *Chemistry* (Pitman).

The interest shown in the preparation of this book by Mr. T. Sommerville, Director of Education, Montreal Protestant Central School Board, is also gratefully acknowledged.

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June 18, 1946.

Chapter 1

INTRODUCTION

1. What is Chemistry?

Chemistry is the science which deals with all kinds of materials and the changes which these materials undergo. Every day wonderful changes in substances take place all around us. Nearly all metals tend to rust, losing their bright lustre and changing into material that looks like earth rather than metal. Coal, wood and oil burn to produce gases and ashes. Again, in the automobile engine, gasoline burns to give great quantities of gases, but we are usually more interested in the motion of the car than in these changes in the gasoline. In nature we find that growing plants take up materials from the soil and the air to manufacture the vast number of things which man secures from plants and trees. Medical science has shown that the food which we digest is used partly to give the body energy and warmth and partly for the building of bones, muscles and other structures of the body. The production of plastics, synthetic rubber, perfumes, cosmetics, paints, explosives, drugs and many other useful products is due to the work of chemists. In fact, the chemist has today some part in the discovery and production of every material used by man, and thus when we seek information regarding any kind of material, we go to him.

Chemists have worked out a way of looking at any problem concerning materials in a systematic manner and they strive to report their results in clear and simple language. It should be the aim of students of chemistry to get this *point of view* and to become masters of the *technical language* which chemists use in stating and discussing their results.

2. Nature Supplies Man with Raw Materials

Every material of service to civilized man comes originally from nature; namely, from the air, the rocks and the soil. In this way we get the metals of the workshop, the drugs used in medicine, the chemicals of the laboratory, the clothes we wear, the food we eat and the furnishings of our homes. As a rule the chemist works with materials which are not living. He makes use of all the minerals supplied by nature and he also employs many products of living things, such as fats, sugars, starches and hundreds of other substances. Starting with these he has produced countless new materials which are very useful to man. From the rocks he has prepared a large number of metals and such necessary things as lime, cement, fertilizers and pigments. From coal he has manufactured dyes, drugs, fertilizers, fuel and many less familiar materials.

3. The Work of the Chemist

There are two different sides to the work of the chemist. He may be eager to discover the "why" of all the changes which materials undergo; why metals rust in the air; why gunpowder explodes; why some soils grow crops while others do not; why cement hardens when we wet it. Such a man has a great desire to find out facts and organize his knowledge in an orderly way into a science. He is called a *research chemist* and his work consists of pushing out beyond the boundaries of what is already known.

Courtesy of Canadian Industries Ltd.

FIG. 1

A research chemist examines the crystal formation of salt under the laboratory microscope.

Some chemists, on the other hand, are more interested in applying chemical knowledge to practical problems. They are anxious to know how to make better or cheaper steel, or matches, or glue, or a drug which will cure a certain disease. They are known as *industrial chemists* and many of them are trained as chemical engineers. Most chemists are interested in both of these tasks, and the work of each helps the other.

4. Chemical Industries

Almost all the industries which change a raw material into a finished product for human use could be classed as chemical industries. All such industries depend upon the principles of chemical science, and should be supervised by men who understand chemistry. Soap, matches, cement, explosives, photographic materials, paints, metals, glass, synthetic rubber, plastics, nylon, acids and chemicals are a few of the useful materials produced by chemical industries.

Courtesy of Aluminum Co. of Canada, Ltd.

FIG. 2—MODERN INDUSTRIAL CHEMICAL LABORATORY

These applications of chemical science are sufficient to show us that it is most closely connected with everyday life. A great scientist has said: "In our century science is the soul of the prosperity of nations and the living source of all progress. What really leads us forward are a few scientific discoveries and their application."

EXERCISES

1. (a) Define chemistry.
   (b) What should be the two aims of students of chemistry?
2. (a) What are the chief raw materials used by chemists in supplying the needs of man?
   (b) Tabulate ten substances produced from the raw materials mentioned in 2(a).
3. Write a short note on the work of the chemist.
4. Tabulate ten chemical industries.

Chapter II

MATTER AND ITS BEHAVIOUR

1. Matter and Energy

In the previous chapter it was stated that chemistry is the science which deals with materials and the changes which materials undergo. The chemist uses the term *matter* instead of the word *material.* Now, it is important to know that in scientific work the terms used always have a definite meaning and one should always be sure that the exact meaning of the terms used is known. The term *matter* is defined as *anything which has weight and occupies space.* As a rule, matter may be perceived by the sense of touch and *it is recognized by its properties or qualities.*

In the world of science it is believed that the universe consists of matter and energy. *Energy* is defined as the *capacity to do work.* Work here means the action of a force in motion. The common forms of energy are: mechanical, electrical, chemical, heat and light. From everyday experience it is observed that these forms of energy can be transformed from one to another. Since energy is always associated with matter, the latter is often called the vehicle of energy.

The chemist is concerned chiefly with matter and its changes, while the physicist is more concerned with energy and the transformation of one kind of energy into other kinds. Since energy is always associated with matter, and since energy changes always accompany chemical changes, the chemist is also much concerned with energy.

2. The States of Matter.

Matter exists in *three* states: the solid, the liquid and the gaseous. Solids are substances which have definite volume and definite shape. Liquids have definite volume but they do not possess definite shape. Gases

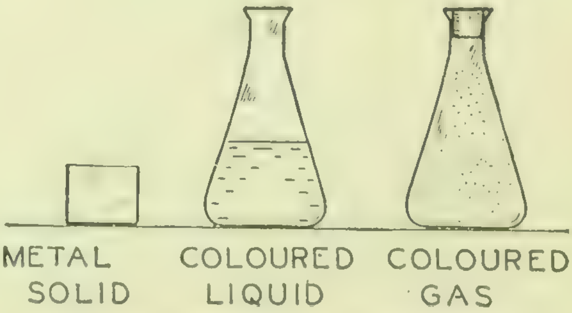


Fig. 3—Three States of Matter

have neither definite volume nor definite shape. Solids and liquids are visible to the eye but, as a rule, gases are invisible. There are a few gases which can be seen, such as chlorine and nitrogen dioxide.

The states of matter depend on *temperature* and *pressure.* Thus water exists as ice, liquid and vapour (gas). Ice and liquid water are visible, but water vapour or steam is invisible. This may be observed by watching water boiling in a tea-kettle; near the spout nothing is visible, but farther away there is a cloud which consists of droplets of liquid formed by the condensation of the water vapour. Invisible water vapour is a normal component of the air we breathe, which is never dry. The air can be changed to a liquid, which is known as liquid air, by subjecting it to much cooling and great pressure. These examples illustrate the idea that the two factors which regulate the states of matter are temperature and pressure.

Many solids change to a liquid when heated and this change of state is called *melting.* When a liquid is heated it is changed to a gas or vapour and this process is known as *evaporation.* Some gases on cooling at ordinary pressure are converted to the liquid state and this is known as *condensation.* Liquids can be changed to solids by cooling and this change of state is called *freezing* or *solidification.*

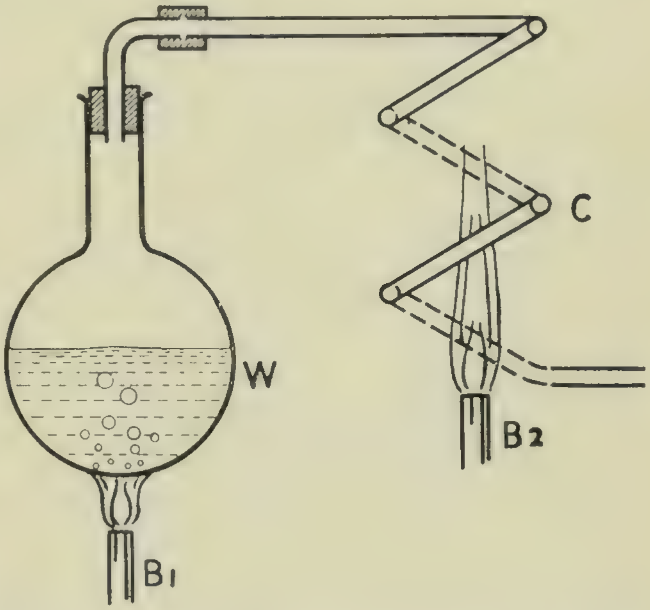


Fig. 4—Apparatus to Show Steam to be Invisible

W—Water; C—Copper Coil; B1—First Bunsen Burner; B2—Second Bunsen Burner.

These changes of state are familiar to all, but there is another change of state, called *sublimation*, which is not so well known to the average person. Sublimation is defined as the direct change from the solid to the gaseous state without going through the liquid state. A good example of this process is the decrease in size or disappearance of moth balls when left in a trunk of clothes for a long time. Iodine crystals also sublime readily to a purple vapour when heated gently.

3. The Molecular Theory of Matter

The scientist is not satisfied with discovering facts alone but he attempts to explain his observations by means of a mental picture or assumption called a theory. The molecular theory of matter is one of the most important in chemistry and physics and it has been of great assistance in explaining facts and laws.

The chief points of this theory are as follows:

(1) All materials are composed of very small particles called *molecules.*

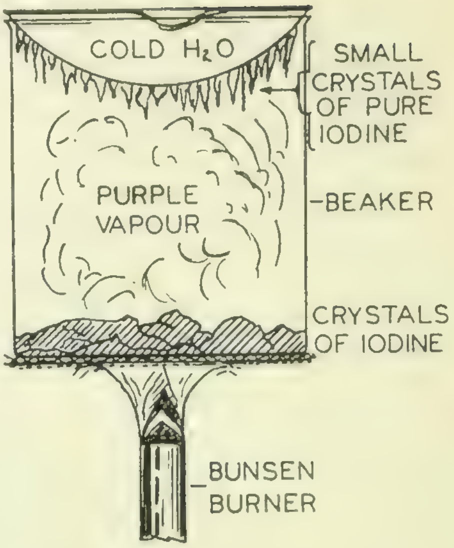


Fig. 5—Sublimation of Iodine

(2) These molecules are *invisible* and cannot be seen even with the aid of the most powerful microscope. It has been calculated that 1 c.c. (about one-third of a thimble) of air contains about 30,000,000,000,000,000,000 (3×10^{19}) molecules.

(3) There are spaces between the molecules which are supposed to be much larger than the molecules themselves. These spaces are called the *inter-molecular spaces.*

(4) Molecules have *kinetic energy* and they are always *in motion.* For this reason this theory is sometimes called the *kinetic molecular theory.* The word kinetic is derived from the Greek meaning *to move.*

(5) Molecules are *elastic.*

(6) Molecules possess a force of attraction for other molecules and this force is known as *molecular attraction.*

This theory concerning matter can be used to explain the differences between gases, liquids and solids. In gases the molecules are quite separate and distinct. They have great freedom of movement and their velocity is much greater than that of liquid or solid molecules. The particles of a gas appear to be perfectly elastic, and as a result their motion is not slowed up when they collide with one another or when they bombard the sides of the enclosing vessel. The pressure of a gas upon the vessel is due to the sum of all the hittings or bombardments of the molecules against the walls of the containing vessel. A definite portion of a gas left in an open container is capable of indefinite expansion due to the high velocity of the molecules. Gases are also very compressible because of the large intermolecular spaces between their molecules. To illustrate: when a quart of water is evaporated it yields about seventeen hundred quarts of steam, measured under normal atmospheric pressure (average pressure of air at sea level) and at the boiling point of water. This shows us why a strong vessel is needed to hold steam at high pressure.

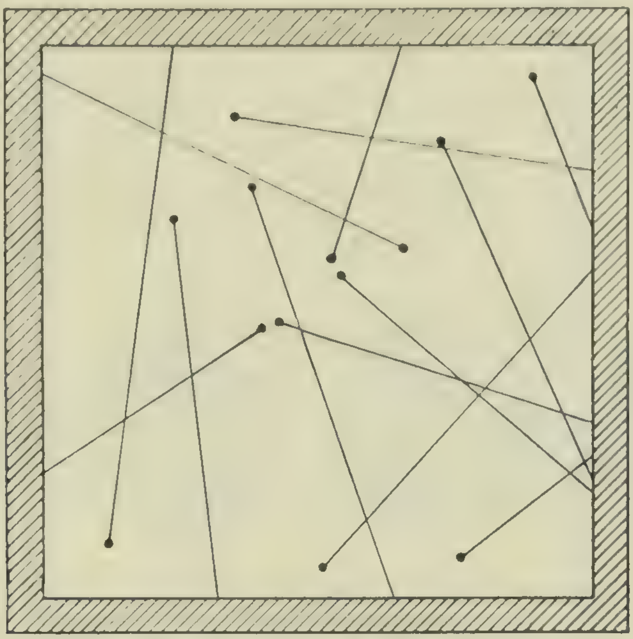


Fig. 6

Diagrammatic representation of the molecules in a Gas to show the cause of Gas Pressure.

A liquid is more compact than a gas; that is, its molecules are closer to one another and therefore have less freedom of movement than gas molecules. Matter in the liquid state takes the shape of the containing vessel. Some molecules of a liquid have

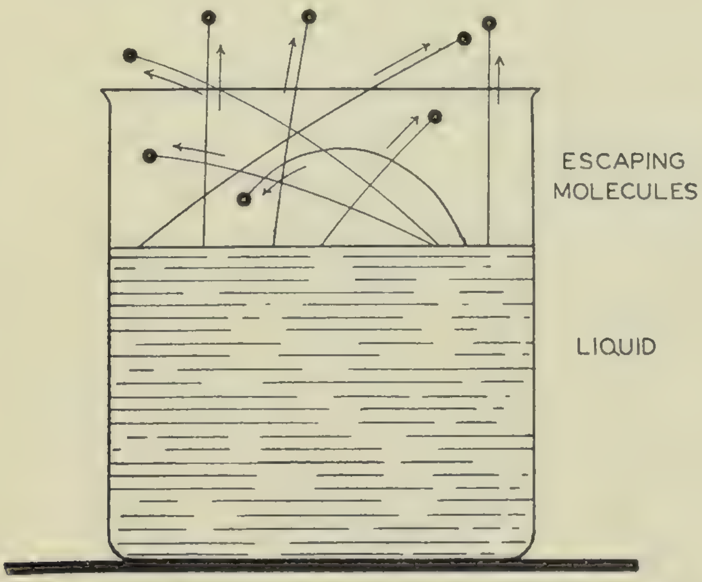


Fig. 7—Evaporation of a Liquid

more energy than others, and these more energetic molecules move up to occupy the surface layer of the liquid. These molecules which make up the surface layer still have enough energy left to pull themselves away from the molecules below them and they escape into the air. In the air the molecules have a great deal of freedom and they are now in the gaseous state. Thus, the theory of molecules explains the evaporation of liquids. The speed of a molecule depends upon its temperature; hence the warmer molecules of a liquid escape first, resulting in a fall in temperature of the liquid on evaporation. It is well known that water is cooled in certain countries by placing it in porous vessels in order to promote evaporation.

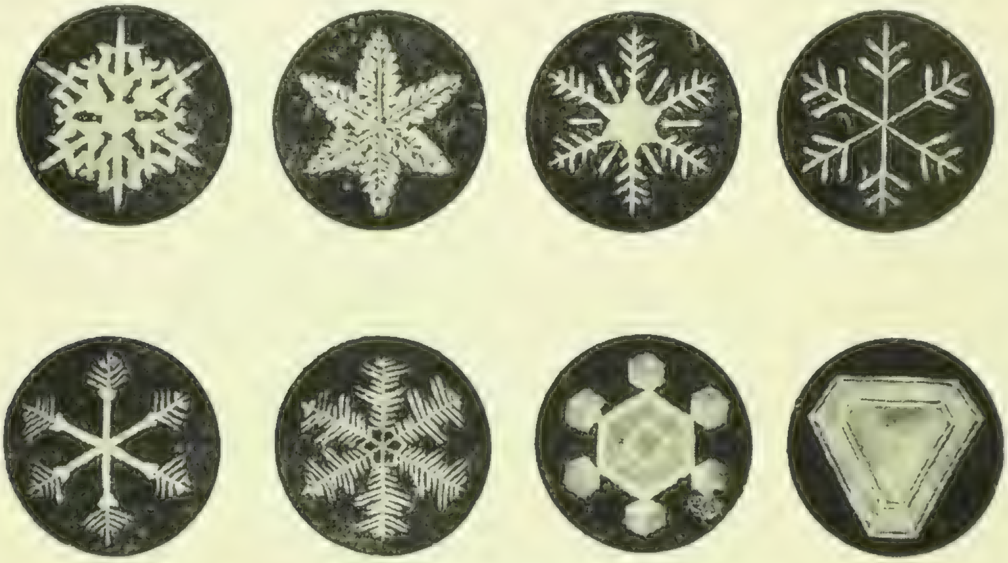


Fig. 8—Some Snowflakes

A solid body retains or tends to retain any form imposed upon it by nature or by art. Solids, like liquids, are much more compact than gases. The molecules of solids are much restricted in their movements, and they appear to vibrate or rotate about centres of rest. Sometimes the particles of which a piece of solid matter is composed have no definite form, and even under the microscope show no sharp edges or flat surfaces. Such solids are said to be *amorphous*. More often a careful examination of a solid will show that it is made up of a great many particles, each of which has sharp edges and flat surfaces. Such solids are said to be *crystalline* and each individual piece is called a *crystal*. Crystals have a great variety of forms but for any given substance the crystalline form is perfectly definite. Crystals range in size from microscopic to very large. It has been reported that crystals of the mineral beryl have been found that are from twelve to fourteen feet long and from two to three feet in diameter.

EXERCISES

1. Colourless gases are invisible. Why are they called matter? Do you know anything which may be seen that is not matter?
2. (a) Define the terms matter and energy.
   (b) Why is the chemist concerned with energy?
3. (a) Define the three states of matter.
   (b) What factors regulate the states of matter?
   (c) Define: evaporation, melting, condensation, sublimation, freezing.
4. (a) What is a scientific theory?
   (b) Tabulate the chief points of the molecular theory of matter.
5. Explain the evaporation of liquids and the pressure of gases in terms of molecules.
6. Discuss the differences between gases, liquids and solids from the viewpoint of the molecular theory.
7. How many quarts of steam would 5 gallons of water produce?

Chapter III

UNITS AND MEASUREMENTS

1. Measurements

Real progress in scientific work is only accomplished when exact measurements are made. It is well for the beginner in any branch of science to take much care in making measurements in the laboratory and to record the data so obtained in a neat and careful manner. *Every measurement is essentially a comparison.* A quantity to be measured is compared with another quantity of the same kind, called the unit. Thus, to measure a length it is necessary to find *how many times the unit of length is contained in the given length.* For example, we speak of a length being five feet, the unit selected being a *foot,* and the number five expressing the number of times the unit is contained in the given length.

The unit must be of the same nature as the quantity which is to be measured, since *only like things can be compared.* There must, therefore, be as many different kinds of units as there are kinds of quantities to be measured.

2. Fundamental Units

There are three units which are known as fundamental. These are the units of *length, mass,* and *time.* Furthermore, it has been found that the measurement of any quantity, such as the power of a steam engine, the speed of a rifle bullet or the strength of an electric current, can be reduced to measurements of length, mass and time.

3. The English and the C.G.S. Systems

There are two widely used systems of units, namely, the English and the C.G.S. In the former, the *foot,* the *pound* and the *second* are the units of length, mass and time, respectively. In the latter, which is used in scientific work, the units of length, mass and time are the *centimetre,* the *gram* and the *second,* respectively. The English system is sometimes known as the F.P.S. system and the other as the C.G.S. system, the distinguishing letters being the initials of the units of the two systems.

4. Units of Length

The unit of length in the C.G.S. system is the *centimetre,* or one-hundredth part of a metre. The metre is the distance between the ends of a bar of platinum which is kept in Paris.

In the metric system the units are divided and multiplied decimally. The names of the sub-divisions are obtained by using the Latin prefixes, *deci* (1/10), *centi* (1/100), *milli* (1/1000), and the names of the multiples are formed with the Greek prefixes, *deca* (10), *hecto* (100), *kilo* (1000). Thus:

10 millimetres (mm.) = 1 centimetre
10 centimetres (cm.) = 1 decimetre
10 decimetres (dm.) = 1 metre
1000 metres (m.) = 1 kilometre (km.)

The English standard of length from which the foot and inch are determined is the standard yard, which is kept in London, England. The relation between the metre and the inch is:

1 metre = 39.37 inches

From this relationship we can calculate that:

1 inch = 2.54 cm.
1 foot = 30.48 cm.
1 mile = 1.61 km.

5. Units of Area and of Volume

The ordinary units of surface area and of volume are derived from the units of length. Thus, we have the square metre (sq. m.), the square centimetre (sq. cm.), the square foot (sq. ft.), the square yard (sq. yd.) etc.; also, the cubic metre (cu. m.), *the cubic centimetre* (c.c.), the cubic inch (cu. in.), the cubic foot (cu. ft.) and so forth. *The cubic decimetre, which contains 1000 cubic centimetres (c.c.) is called a litre* and this unit of volume is used a great deal in chemistry.

6. Unit of Mass

By the *mass* of a body is meant the *quantity of matter* in it. Matter may change its form, but it can never be destroyed. A sample of matter may be transported to any place in the universe, but its mass will remain the same.

The unit of mass in the C.G.S. system is the *gram,* or one-thousandth part of the standard kilogram, which is a mass of platinum kept at Paris. The standard kilogram was intended to represent the exact mass of a cubic decimetre of pure water at its greatest density or at a temperature of 4° on the Centigrade thermometer scale.

The gram is, therefore, equal to the mass of a cubic centimetre of pure water at 4° Centigrade. This relation between the cubic centimetre and the gram is very useful, because it enables us to determine the volume of an irregular vessel from the weight of water which it can contain. The kilogram is divided decimally as follows:

10 milligrams (mg.) = 1 centigram
10 centigrams (dg.) = 1 decigram
10 decigrams (dg.) = 1 gram
1000 grams (gm.) = 1 kilogram (kg.)

The English unit of mass is the *pound avoirdupois* which is a certain piece of platinum kept in London, England.

1 kg. = 2.21 lbs.
1 oz. = 28.35 gms.

To find the mass of a small object, we use the balance. This apparatus is one of the most important tools of the chemist and it really compares the weights of different objects. Since, however, the weight of a body is proportional to its mass, we may say that two objects which balance each other in weight are equal in mass.

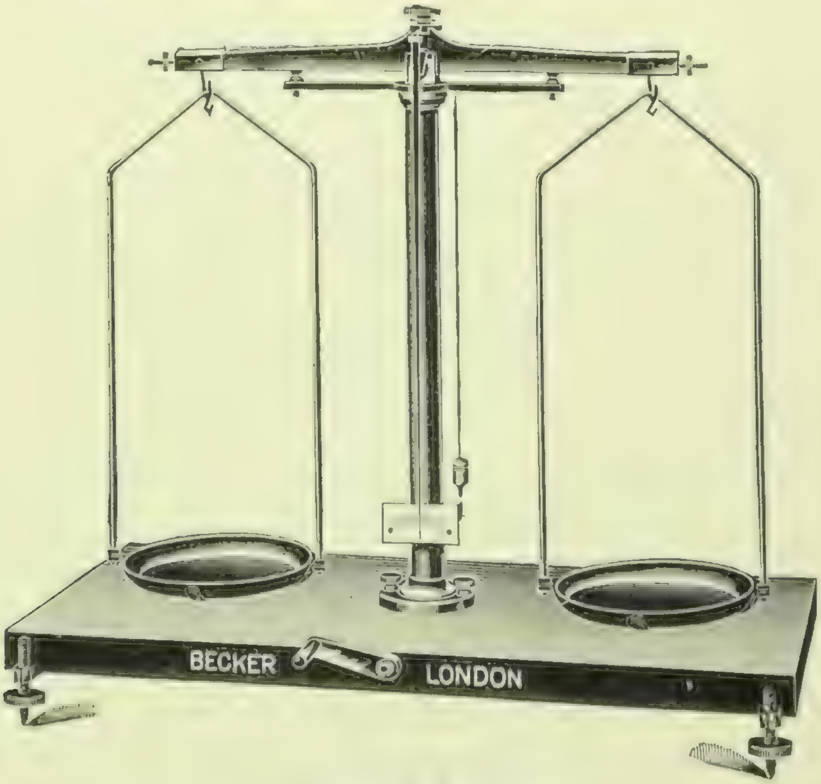


Fig. 9—A Balance

7. Unit of Time

If we reckon from the time when the sun is on our meridian (noon), until it is on the meridian again, the interval is known as a *solar* day. However, the solar days thus determined are not all exactly equal to one another. The reason for this will be found in books on astronomy. The average length of the solar days is called the *mean solar day.* The ordinary standard time used in everyday life is mean solar time.

The unit of time is the *mean solar second*, which is 86,400th part of a mean solar day. It is used in science as the fundamental unit of time.

EXERCISES

1. How many millimetres are there in 2.5 kilometres?
2. Light travels 186,330 miles in a second; express this in kilometres.
3. The floor of a building is 13 metres wide and 30 metres in length; how many square centimetres are there in it?
4. Hydrogen weighs 0.09 grams per litre. Calculate the weight of 22.4 litres of this gas.
5. Express, correct to a hundredth of a millimetre, the difference between 12 inches and 30 centimetres.

CHAPTER IV

PHYSICAL AND CHEMICAL CHANGES

1. Introduction

It is a familiar fact that things are always changing. In certain cases the changes are very slow, as in the rusting of steel. This change alone, however, costs millions of dollars annually. Other changes, such as the combustion of fuel, are rapid and are often accompanied by the evolution of *heat* and *light*. All the changes which matter undergoes can be classified into two kinds, physical and chemical. It is well to remember, however, that some changes observed in nature or in everyday life cannot be clearly defined as a physical or a chemical change. For instance, the weathering of rocks to produce clay is brought about by both physical and chemical changes. The physical changes caused by the alternate freezing and thawing of water in the pores and crevices of rocks is accompanied by chemical changes due to the action of carbon dioxide and water.

2. Physical Changes

There are many changes which are more or less *temporary* and they do not involve the transformation of the body or material into a new substance having essentially different proper-

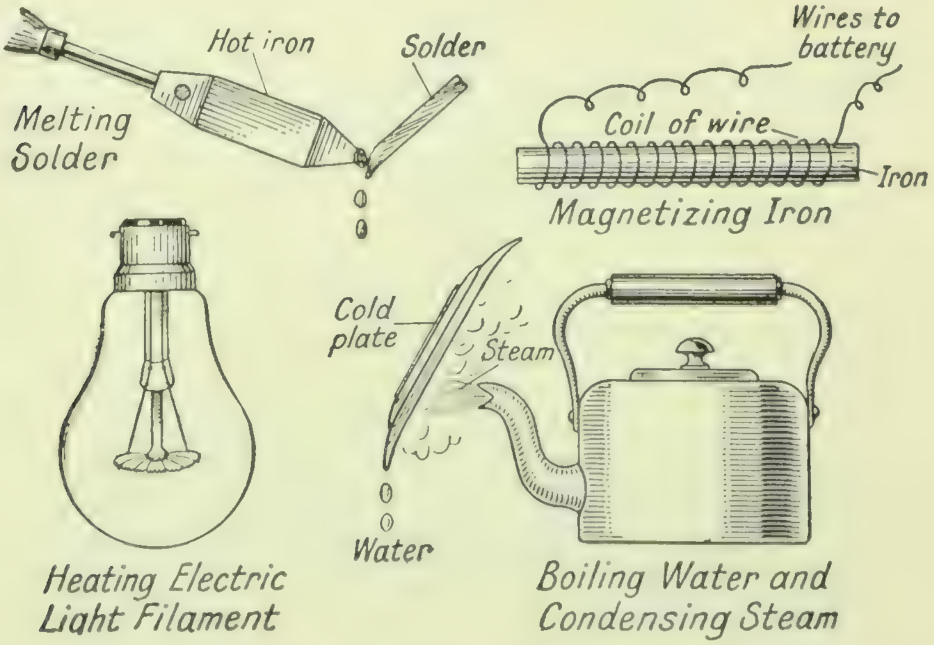
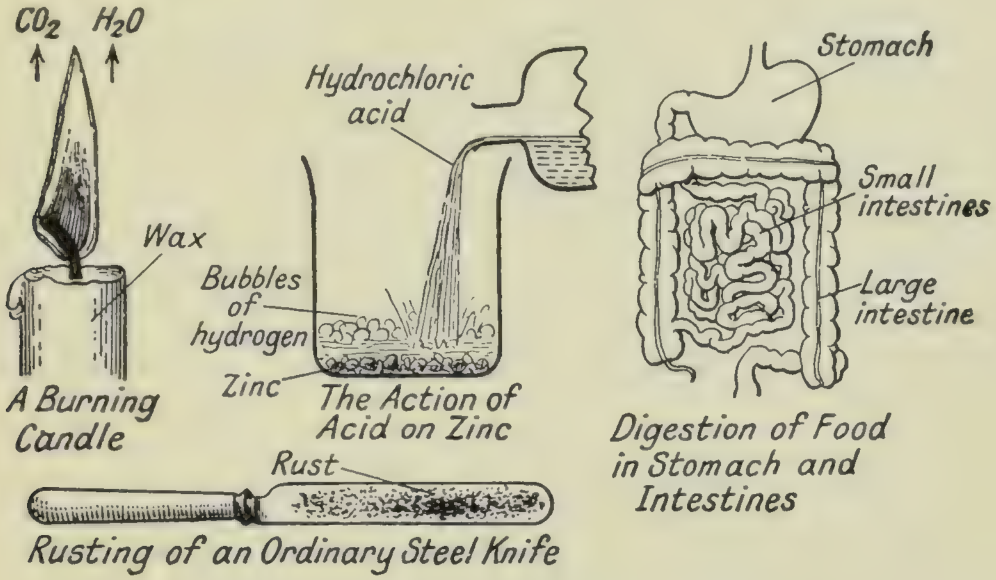


FIG. 10—SOME PHYSICAL CHANGES

ties. In terms of the molecular theory we can say that *no new molecules* are formed. Changes of this kind are called *physical changes.* Familiar illustrations are the magnetization and heating of iron, the crushing of stone, and the formation of dew and frost.

3. Chemical Changes

Many changes which occur involve the transformation of various forms of matter into other substances possessing very different properties. These changes are *permanent.* From the viewpoint of the molecular theory we can state that *new molecules* are produced. Changes of this kind are called *chemical changes.* The souring of milk, the combustion of fuels, the decay of animal and vegetable matter, the breaking down of explosives and the corrosion of metals are examples of chemical change. Changes of this kind are called chemical changes because the chemical composition of the various materials is altered. Iron, for example, is changed on exposure to the air into iron rust, which is known as iron oxide by the chemist. When a fuel burns it can be shown by experiment that water and carbon dioxide gas are the chief products. The corrosion of metals, the production of animal heat, and change and decay in general are largely dependent upon the oxygen of the air. Large quantities of paints and varnishes are applied to metals and wood to protect these materials from slow but sure destruction by the action of the atmosphere. When a big gun is fired, a chemical change



A Burning Candle

The Action of Acid on Zinc

Digestion of Food in Stomach and Intestines

Rusting of an Ordinary Steel Knife

FIG. 11—SOME CHEMICAL CHANGES

on a large scale takes place and huge quantities of nitrogen and other gases are liberated.

4. A Chemical Reaction

The term chemical reaction is often used instead of chemical change and it is important to remember that a chemical reaction is always accompanied by the production or using up of some form of energy such as heat, light or electricity.

5. The Law of Conservation of Mass

In science we find that there are certain statements of facts which we can show to be true by observation or by experiment. These statements of facts are known as scientific laws. The *Law of Conservation of Mass* is a very important chemical law. It is sometimes also called the *Law of Conservation of Matter* and it can be stated in several ways. Chemists usually state it as follows: *The sum of all the weights of all the starting materials taking part in a chemical reaction always equals the sum of the weights of all the products of the reaction.*

In physics the law is usually stated thus: *Matter can neither be created nor destroyed.* The truth of this law can be demonstrated in the laboratory by bringing about a chemical reaction in a closed system. The system is weighed before and after the reaction takes place and the two weights should be the same.

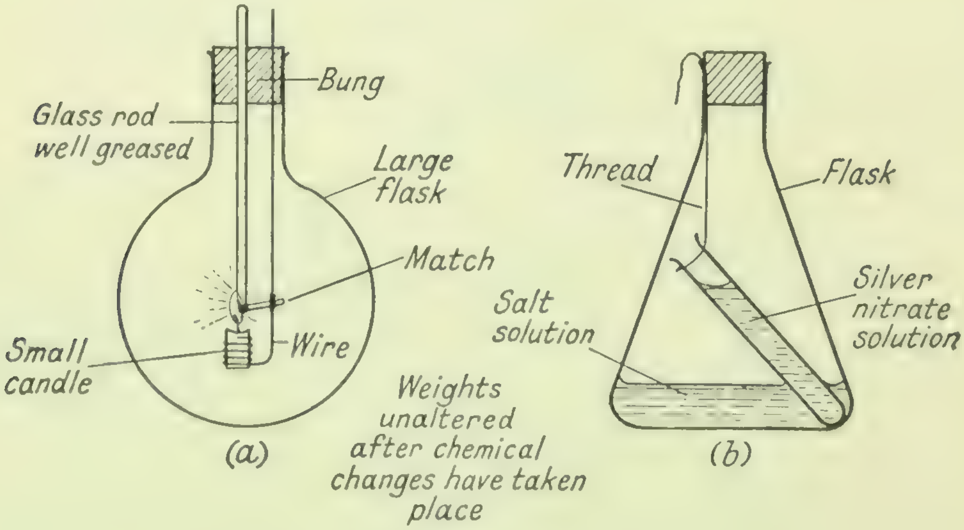


Fig. 12—Matter is Indestructible

EXERCISES

1. (a) Distinguish between physical and chemical changes.
   (b) Give three examples of each.

2. If we pound iron it becomes hot. Have we produced a chemical change?
3. If we scratch a match on a box we produce both heat and light. Is this a chemical change? Give your reasons.
4. What forms of energy are usually produced in a chemical change?
5. (a) What is meant by a law in science?
   (b) State the Law of Conservation of Mass and discuss its importance in chemistry.

CHAPTER V

THE PROPERTIES OF MATTER

1. How Do We Recognize Materials?

No one would have any difficulty in telling the difference between a block of wood and a bar of iron, even if the piece of wood were painted black. Wood floats on water, while iron will not. A magnet attracts a piece of iron but it will not attract a stick of wood. Wood burns readily in air, whereas iron does not. Such characteristic facts about a given material are called its *properties*. Any particular material can be recognized and identified by knowing a number of its properties.

2. Measurable Properties

Many properties of materials can be determined accurately and expressed by numbers. For example, the mass (weight) of a unit volume of a material is known as its *density*. In scientific work, the density of a substance is considered to be the weight of one cubic centimetre. In industry, density is the weight of one cubic foot of a material. In the case of gases, the density is usually the weight of *one litre* under certain standard conditions of temperature and pressure.

The densities of some common substances are given in the table below.

TABLE 1—DENSITIES OF SOME COMMON SUBSTANCES
(In grams per cubic centimetre)

Water (pure)	1.00
Sea water	1.03
Wood Alcohol	0.81
Sulphuric Acid	1.84
Kerosene	0.88
Gasoline, about	0.70
Mercury	13.60
Aluminum	2.70
Butter	0.86
Chalk	2.40
Copper	8.90
Glass (ordinary)	2.69
Diamond	3.50
Tungsten	19.30
Potassium	0.86
Calcium	1.55
Magnesium	1.74
Gold	19.34
Ice	0.90
Iron	7.85
Lead	11.34
Paper (average)	0.90
Platinum	21.45
Silver	10.50
Zinc	7.14
Cork (average)	0.24
Birch wood (average)	0.64
Cedar (average)	0.53
Maple (average)	0.68
Oak (average)	0.75
White Pine	0.42
Sodium	0.97
Tin	7.31
Chromium	7.10

Some substances are harder than others, and the hardness of substances can be compared quite accurately. A diamond is the hardest substance known, as it will scratch all other solids. Many substances melt at a higher or lower temperature than others, and some materials are often distinguished by this means.

Thermometers have been invented by scientists to measure accurately such properties as boiling points, freezing points and melting points. In the *Centigrade thermometer* the freezing point of pure water is marked 0 degrees, while the point on the thermometer which records the temperature at which water boils at sea level is marked 100 degrees. The space between these two points on the thermometer is divided into 100 equal divisions. The Centigrade thermometer is used in all scientific work. The *Fahrenheit thermometer*, ordinarily used in our homes and in industry, has the freezing point marked 32 and the boiling point marked 212 with the space between divided into 180 equal divisions.

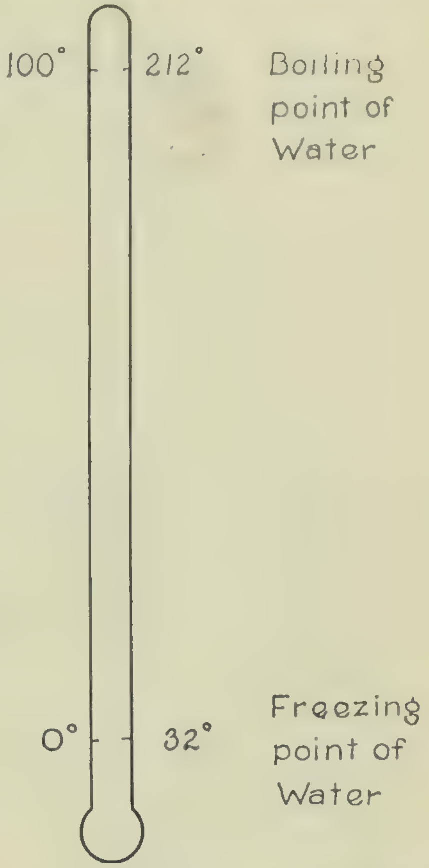
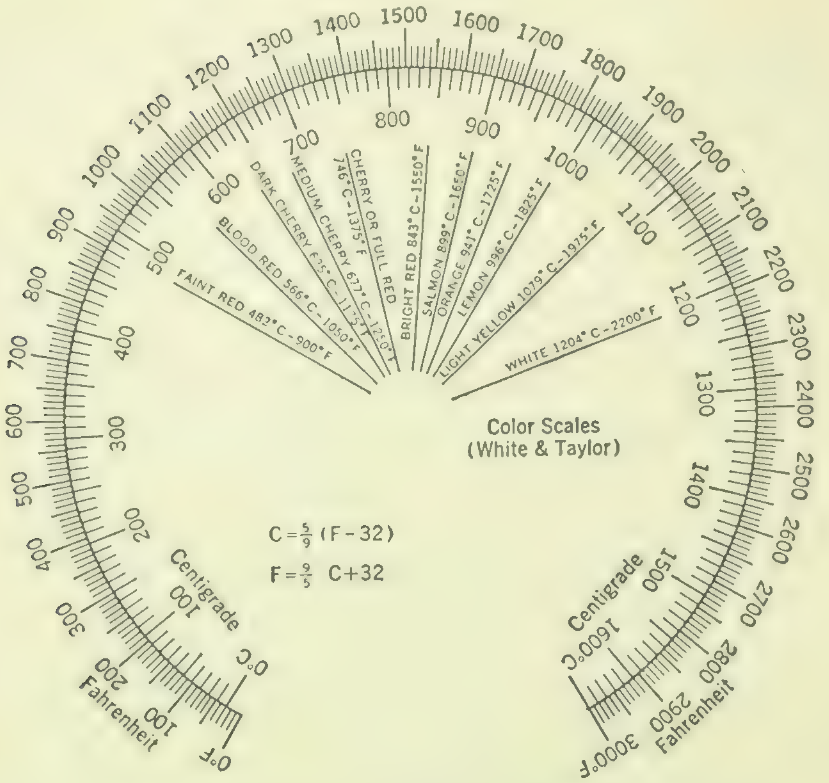


FIG. 13—ONE THERMOMETER MAY CARRY BOTH CENTIGRADE AND FAHRENHEIT SCALES

3. Physical Properties

Chemists have classified all properties of materials into two kinds, *physical* and *chemical*. The physical properties of a substance are those which are usually observed by means of our bodily senses, such as our senses of sight, touch and smell. For example, the colour of an object is a physical property and its weight is also a physical property. *The physical property of a substance is a fact about the material which does not suggest a chemical change.* Again, it can be said that the physical properties are what it is like, meaning by this its physical state (whether it is a solid, a liquid or a gas), its colour, odour, taste, melting point, boiling point, hardness, density, and any other properties of the substance which do not involve any change in its chemical composition.

There are a great many physical properties and so we usually



Courtesy of Canadian Johns-Manville Co. Ltd.

FIG. 14—A CENTIGRADE-FAHRENHEIT SCALE CONVERSION CHART, SHOWING THE TEMPERATURES AT WHICH A SOLID BODY MAY ASSUME VARIOUS COLOURS WHEN HEATED

try to remember only a few of the more important ones. The physical properties that we usually study are *colour*, *odour*, *weight* and *solubility*. The one word *cows* will help us to remember these.

C — stands for Colour
O — " " Odour
W — " " Weight
S — " " Solubility

Copper sulphate or blue stone has a blue colour when observed in large crystals but grinding these crystals changes the colour to a much lighter shade of blue. This illustration indicates that colour is not always a reliable property to be used in identifying a substance.

Gases may be poisonous or they may have a disagreeable odour; hence, the odour should be detected in a careful and cautious manner. It is well to hold the container of the gas about a foot away from and a foot below the nose and with your free hand waft the air just above the open vessel. In this way, only a gentle whiff of the gas is obtained.

If a substance is a gas it is customary to compare its weight with an equal volume of air under the same conditions. For example, oxygen is slightly heavier than air, whereas hydrogen is about fourteen times lighter than air. In the case of liquids or solids we compare their weights with that of an equal volume of water at the same temperature. Thus, iron is about eight times as heavy as an equal volume of water.

The solubility of a substance is a property which certain materials possess of disappearing into some other substance. For example, when two grams of common salt is mixed carefully with 25 c.c. of water it is observed that the salt disappears completely in the water. The chemist describes this fact by saying that the salt *dissolves* in the water and he calls the resulting mixture a *solution.* He calls the dissolving liquid (water) the *solvent*, and the dissolved substance (salt) is known as the *solute.* The salt is said to be soluble in water and this property of the salt to dissolve in water is called its *solubility.* Many of the materials encountered in everyday life are soluble in water, at least to some extent. Some substances are practically insoluble, such as the metals, rocks, glass and cement. Other fluids, such as alcohol and gasoline, are also good solvents especially for such things as fats, oils, and waxes. However, water is by far the most general solvent for all classes of substances.

4. Chemical Properties

It is a chemical property of iron to rust when exposed to moist air. In rusting, iron is converted into a different substance, namely rust, which the chemist calls iron oxide. Rust possesses properties which are quite different from those of iron. A chemical property of wood is that it will burn. These two examples attempt to illustrate the idea of the chemical properties of a substance. Thus, *the chemical properties of a substance imply that it can undergo a chemical change.* Perhaps the best way to study the chemical properties of any substance is to ask yourself questions concerning it. For example, if the material under consideration is a gas we could ask certain leading questions about it. Does it burn? Does it explode? Does it cause a glowing splinter of wood to burst into flame? The correct answer to such questions would give us a number of chemical properties of the gas. If the substance being considered is a solid, it would be necessary to ask questions different from those asked in regard to gases. Does the solid burn in air or in oxygen? Does it react with the common acids or alkalis? Does it react with certain chemical elements such as sulphur or chlorine?

A study of the physical and chemical properties of any material is important because it is only when we know these facts that industrial uses can be made of any given substance.

EXERCISES

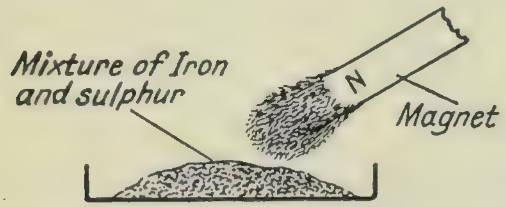
1. If sand and sugar are mixed together, what property of each would you use in separating them?
2. What property would you make use of in distinguishing between:
    (a) Copper wire and iron wire?
    (b) Wood and iron?
    (c) Powdered sugar and flour?
3. Name some property which is common to all materials.
4. (a) Name five physical properties of iron.
    (b) Name two chemical properties of iron.
5. What do we use a thermometer for? Describe the two types of thermometers which are generally used.
6. Define the following: solution, solvent, solute.
7. Name five other liquids besides water which are good solvents.

CHAPTER VI

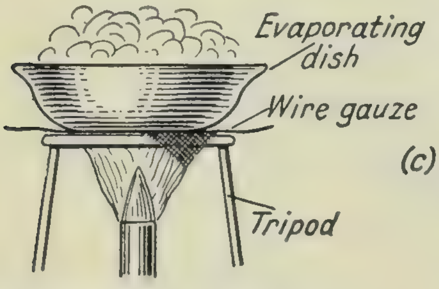
MIXTURES

1. Pure Substances and Mixtures

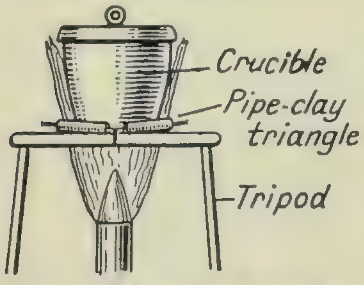
All materials can be divided into two types—pure substances and impure substances. Chemists usually refer to the impure substances as mixtures. A pure substance is one in which every particle of the material is the same as every other particle. In terms of molecules it is a material in which all the molecules are alike. Since a pure substance is homogeneous all parts of it will have exactly the same properties. Every sample of the substance will be found to be exactly like every other sample. For example, pure water will contain only water molecules and no other kind of molecule will be present. Pure sugar will be one hundred per cent sugar and no other material will be associated with it.



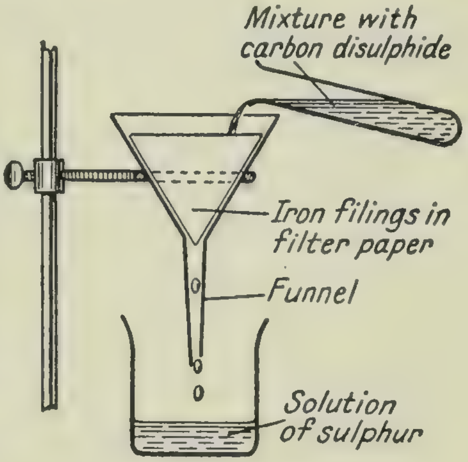
(a) Separating Iron from Sulphur with a Magnet



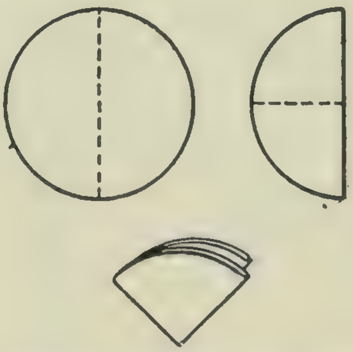
(b) Recovery of Solute from a Solution by Evaporation



(d) Formation of Iron Sulphide by Heating Mixture of Iron and Sulphur



(c) Separation of Iron from Sulphur by dissolving Sulphur in Carbon Disulphide



Method of folding Filter Paper

FIG. 15—MIXTURES AND COMPOUNDS

If a pure substance is mixed with another pure substance we are then dealing with an impure material or a mixture. Of course, the properties of a mixture will depend on how much of each substance is present. For example, a mixture of ten parts of iron and one part of sulphur by weight is grey, while a mixture of ten parts of sulphur and one part of iron by weight is almost pure yellow. The parts of a mixture are called *components*. For example, in a mixture of iron and sulphur the components are iron and sulphur. *A mixture is thus made up of two or more pure substances mixed together and the components of a mixture can usually be separated by physical means.* For example, a mixture of salt and sand can be separated by the addition of water to the mixture. The water dissolves the salt and the sand can be removed by the process of filtration. The sand remains on the filter paper and it is called the *residue*. The salt solution passes through the filter paper and it is known as the *filtrate*. On evaporation of the water from the salt solution, it is observed that the salt is left behind in the evaporating dish. The salt and sand still have their original properties after the separation has been brought about.

2. Methods of Separating Mixtures

(1) FILTRATION. If an *insoluble solid substance* such as powdered gypsum, is mixed with water, the resulting mixture is known as a *suspension*. Fine clay mixed with water, is another good example of a suspension. The insoluble substance can be separated from the water by a process known as *filtration*. This consists of pouring the mixture through some porous substance, such as filter paper. The water supply of a town or city is usually purified by filtration through beds of sand and gravel as illustrated by Fig. 17. Filter-presses are used in certain industrial processes to bring about the separation of insoluble solids from liquids; the liquid is forced through a porous material by mechanical means. Sometimes filtration can be

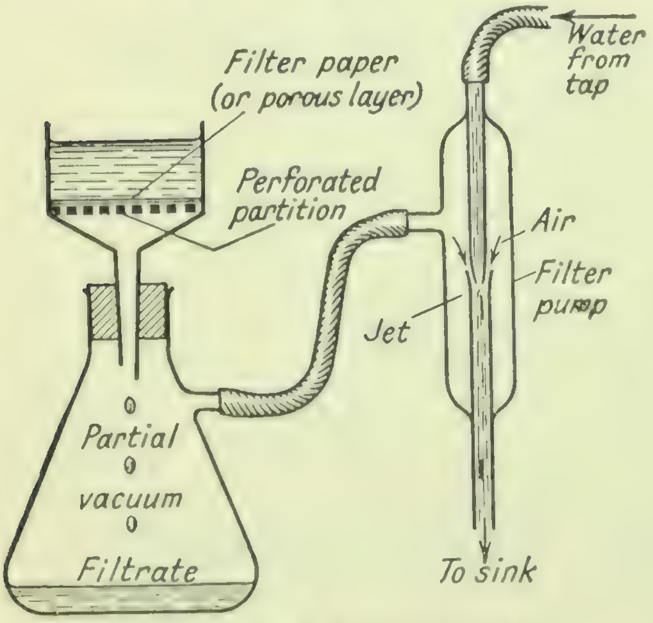


FIG. 16—A FILTER PUMP

speeded up by the use of a filter pump as shown in Fig. 16. Vacuum filters are also used in some industries; the pressure of the air forces the liquid through a porous substance when the air is taken away from the under side of the filter by means of a suction pump.

There are certain suspensions in which the particles are smaller in size than those in an ordinary suspension. Such suspensions are known as *colloidal*, and the solid particles in them are so small that they go through filter paper.

(2) DECANTATION. If an insoluble substance such as sand is mixed with water, the particles of sand will settle to the bottom of the vessel on standing and after a short time the clear water can be removed from the sand by pouring the liquid carefully into another vessel. This process is known as *decantation* and it is often used in the laboratory and in industry.

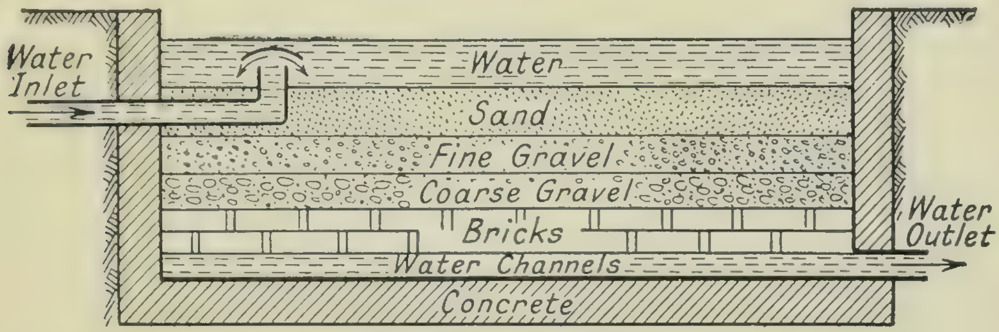


FIG. 17—A FILTER BED

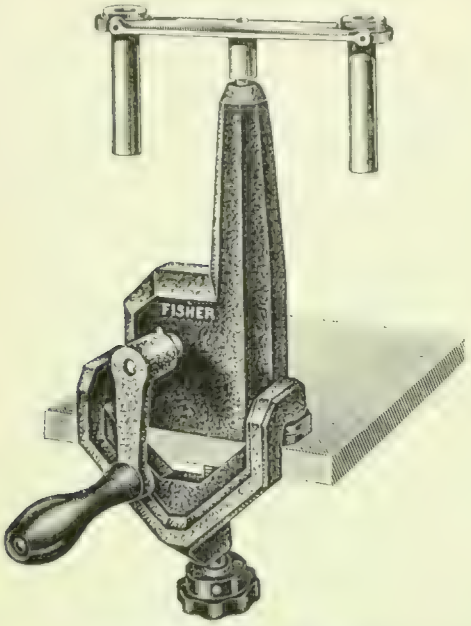
(3) CENTRIFUGE. When very minute droplets of one liquid are suspended in another liquid, we have a type of mixture, known as an *emulsion*. Milk, containing fine droplets of butter fat suspended in water, is a good example of an emulsion. Emulsions can be separated by means of an apparatus, known as the *centrifuge*. A hand driven centrifuge is shown in Fig. 18. However, most of the centrifuges used in laboratories and in industrial processes are driven by electric motors. The principle of the centrifuge is used to separate cream from milk in the cream separator. The centrifuge is also used in the refining of cane sugar.

(4) FLOTATION. This method of separating mixtures is used a great deal in mining operations to separate valuable minerals from useless substances. The rock containing the mineral is ground to a fine powder and then mixed with water to which had been added a small amount of an oil such as pine oil. When the mixture is stirred well the oil produces a froth to which the

mineral particles adhere. The useless substances do not cling to the bubbles of the froth but settle to the bottom of the tank. The froth containing the valuable mineral particles is removed by mechanical means and the oil is readily removed from the mineral particles by heat.

(5) SCREENING. A mixture of solid particles may be separated on the basis of the different sizes of the particles which make up the mixture. Screening depends on the use of woven or perforated material. The holes in these screens allow the smaller particles to pass through but not the larger particles. The sifting of ordinary flour at home in the making of a cake is a good illustration of this process. This method of separation is made use of in the production of flour from wheat.

(6) BY HAND. A mixture consisting of two different types of solid particles could be separated by hand. The great French chemist, Pasteur, used this method in the separation of two different kinds of crystals which he encountered in one of his researches.



Courtesy of Fisher Scientific Co., Ltd.

FIG. 18

A hand driven CENTRIFUGE, used to speed up the separation of a substance suspended in a liquid. If the centrifuge tube is charged with 1 gram of liquid, 16 cm. from the centre of gyration, and is revolving at 2,000 r.p.m., the centrifugal force is about 700 times greater than the force of gravity.

(7) DISTILLATION. A mixture of two liquids which boil at different temperatures can be separated by heating the mixture and cooling the escaping vapours. The liquid with the lowest boiling point will escape first and most of the other liquid will remain behind in the distilling flask. Thus, the two processes of evaporation and condensation are combined to bring about a separation of the two liquids. This process is known as distillation and it is used a great deal in the commercial world.

(8) MAGNETISM. The metals iron, cobalt and nickel are attracted by a magnet. If these substances are mixed with other solids, a separation can be accomplished by the use of a magnet. Thus, a mixture of powdered sulphur and iron filings can be separated by this method.

EXERCISES

1. Write out a clear definition of the following terms: pure substance, mixture, component, filtration, residue, filtrate.
2. Tabulate five methods of separating mixtures and give one example of each method.

CHAPTER VII

CHEMICAL COMPOUNDS

1. What Are Chemical Compounds?

It was discovered in the last chapter that all materials could be classified into two main groups. These were pure substances and impure materials or mixtures. It has been found that all pure substances, in turn, can be divided into two classes, those which are *decomposable* and those which are *undecomposable.* The decomposable pure substances are known as chemical compounds, whereas the undecomposable pure substances are called chemical elements. It can be shown by experiment that pure water can be decomposed by electricity into two very different substances, hydrogen and oxygen. Again, a red powder, known as mercuric oxide, can be decomposed by heat into two quite different materials, mercury and oxygen. Many other examples could be given to show that certain pure substances can be decomposed by heat, light, or electricity into simpler substances. Thus, a *chemical compound can be defined as a pure substance which can be decomposed into two or more simpler substances.*

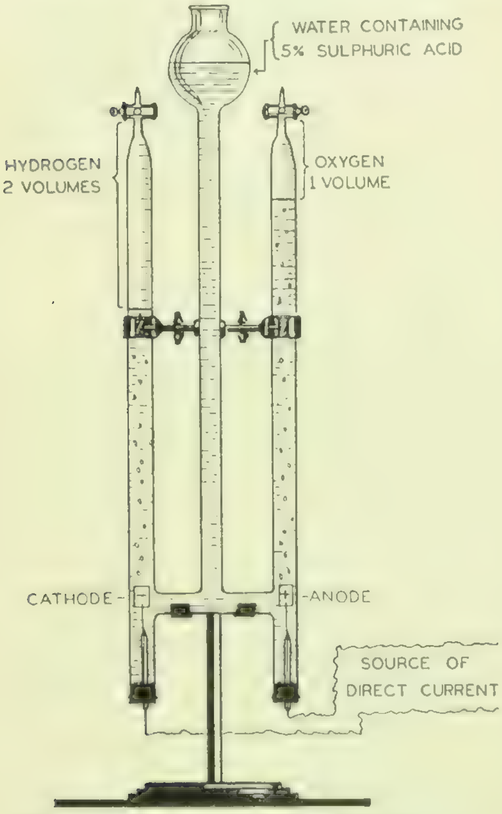


FIG. 19—DECOMPOSING WATER BY ELECTROLYSIS

2. Some Important Compounds

Many compounds play an important role in our everyday lives and they also find many uses in industry. Salt, sugar, lye, sulphuric acid, washing soda, bicarbonate of soda and muriatic acid are examples of common and useful chemical compounds. A table of some important compounds with their common names, chemical names and formulas is given below.

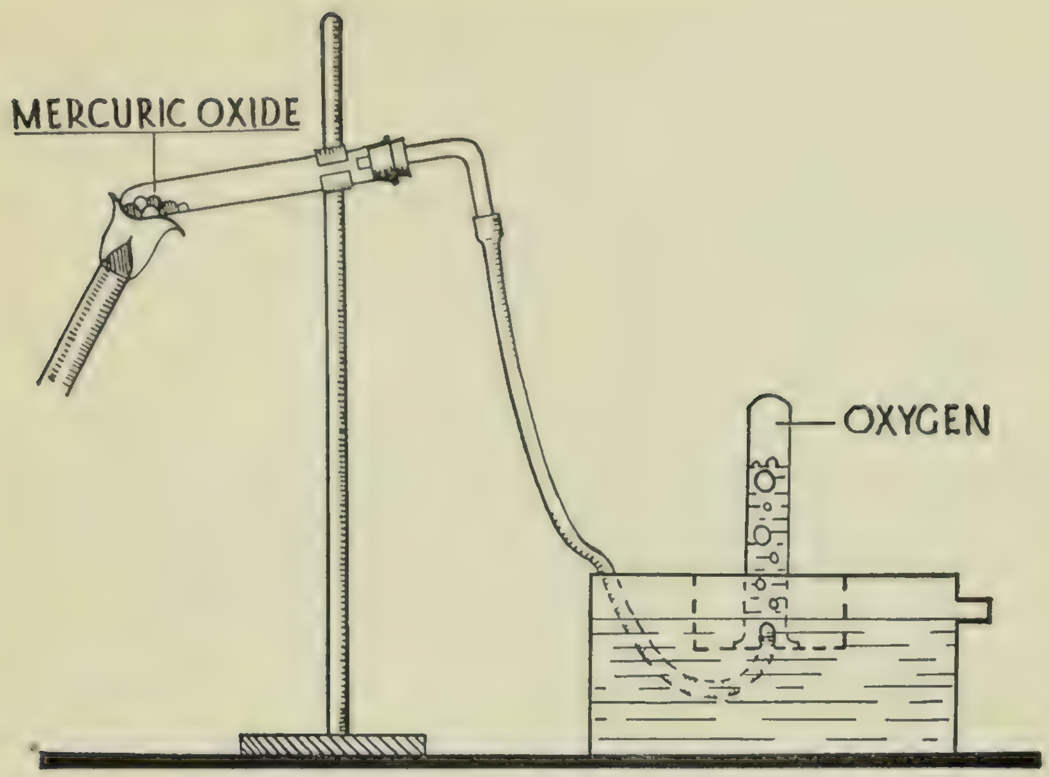


Fig. 20—Decomposing Mercuric Oxide

Table 2—Some Important Compounds

Common Name	Chemical Name	Formula
Common salt	Sodium chloride	$NaCl$
Cane Sugar	Sucrose	$C_{12}H_{22}O_{11}$
Household Ammonia	Ammonium hydroxide	NH_4OH
Lye (Caustic Soda)	Sodium hydroxide	$NaOH$
Alcohol	Ethyl alcohol	C_2H_5OH
Oil of Vitriol	Sulphuric Acid	H_2SO_4
Washing Soda	Sodium carbonate	$Na_2CO_3 . 10H_2O$
Baking Soda (Bicarbonate of Soda)	Sodium bicarbonate	$NaHCO_3$
Saltpetre	Potassium nitrate	KNO_3
Muriatic Acid	Hydrochloric acid	HCl
Limestone	Calcium carbonate	$CaCO_3$
Blue stone	Copper sulphate	$CuSO_4 . 5H_2O$
Javelle water	Sodium hypochlorite	$NaClO$
Vinegar	Acetic Acid	$HC_2H_3O_2$
Chile saltpetre	Sodium Nitrate	$NaNO_3$
Lime-water	Calcium hydroxide	$Ca(OH)_2$
Epsom salts	Magnesium sulphate	$MgSO_4 . 7H_2O$
Calomel	Mercurous chloride	$HgCl$
Sal-ammoniac	Ammonium chloride	NH_4Cl
Quicklime	Calcium oxide	CaO

A formula consists of a group of letters and numbers which represents *one* molecule of a substance. It is well to remember that the molecule is the smallest particle of a substance which can exist by itself in the free state. A student should try to memorize the chemical names and formulas of compounds encountered in the laboratory or in everyday life.

3. Compounds from Elements

The pure substances, which are produced when compounds are decomposed, are known as the *constituents* of the compound. For example, the constituents of cane sugar are carbon, hydrogen and oxygen. These building stones of compounds are also known as chemical elements and they will be considered in detail in the next chapter. When certain elements are combined together in the proper proportions they form chemical compounds. It is a remarkable fact that when elements unite to produce compounds, they lose completely their identity. Common salt is an excellent example of this fact. Salt contains sodium, which is a soft, silvery metal. This metal acts very vigorously with water and it is a dangerous substance to handle. Chlorine, the other constituent of common salt, is a greenish-yellow gas and it is very poisonous. In chemical union, however, these elements lose their own properties to form common table salt, a white, solid compound which is agreeable to the taste and it is needed by the body. Sugar is another good illustration of this important fact that chemical elements lose their characteristic properties when they are combined together to form a compound. Analysis of sugar reveals that it is made up of the elements carbon, hydrogen and oxygen. Everyone is familiar with carbon as black charcoal. Hydrogen burns vigorously and oxygen makes combustible substances burn furiously. Yet when these three elements are combined together in the proper manner they produce a white, crystalline solid which is one of our important foods. When hydrogen and oxygen are mixed together in the proper proportions and exploded, they combine to produce the colourless liquid, water, which puts out fire. In conclusion, *when elements combine to form compounds they lose their own properties to form a new substance with entirely different properties.*

4. The Carbon Compounds

Carbon is the element which enters into the formation of by far the largest number of compounds. It is found in the bodies of all living organisms, and hence the pioneer chemists called the study of the carbon compounds, organic chemistry. At the present time there are over a quarter of a million compounds which contain the element carbon. Many of the organic compounds, such as the sugars, starches, proteins, fats, vitamins, cellulose, alcohol, ether, benzene, and chloroform, are very important. For instance, the starches are the most abundant of foods. Every year research chemists discover many more new organic compounds, and so the number continues to grow from year to year.

5. Compounds Have a Definite Composition

The chemist represents chemical changes, or *reactions*, as they are often called, in a condensed form, thus:

$$\underset{(216)}{\text{Mercuric oxide}} \longrightarrow \underset{(200)}{\text{Mercury}} + \underset{(16)}{\text{Oxygen}}$$

The above is known as a word equation. The arrow (⟶) is read as *yields*, and the plus sign (+) as *and*. The numbers in the parenthesis indicate the *proportions by weight*. Thus, by experiment, it is found that 216 grams of mercuric oxide yields 200 grams of mercury and 16 grams of oxygen. Whatever quantity of mercuric oxide is decomposed, experiments show that 200/216 times 100 or 92.6 per cent of the weight used is left as mercury and 16/216 times 100 or 7.4 per cent of the weight is oxygen.

Many careful experiments have shown that the composition of pure water *by weight* is always 88.8 per cent oxygen and 11.2 per cent hydrogen.

Numerous very careful quantitative experiments show that *every pure compound has a definite composition by weight.* The whole science of chemistry is based on this fundamental fact, which is known as the *Law of Definite Composition.* It is also called the *Law of Definite Proportions.*

6. A Comparison of Mixtures and Compounds

A chemical compound always has a *constant composition.* Thus, common table salt always contains 39.3 per cent of sodium and 60.7 per cent of chlorine, regardless of where it is obtained. A mixture, on the other hand, has a *variable composition.* For example, one can readily prepare a mixture of sand and salt, the amount of each component being varied at will. The sand and salt are in intimate contact, but they are not chemically combined. This fact may be observed by examining the material under a microscope. Furthermore, the two components may be easily separated by the addition of water, in which salt is soluble.

The printed matter on this page illustrates very well the difference between elements, compounds, and mixtures. *The individual letters correspond to the elements.* There are only a few letters but they can be put together in many different ways to form words. *The words correspond to compounds.* Each word has a definite number of letters in it and it is always spelled in the same way. Thus, a word has a definite percentage composition of letters. Both separate letters and words can be mixed in many different ways to make up a great variety of sentences, corresponding to mixtures of elements, compounds, or both.

Some of the chief differences between compounds and mixtures are shown in the table below.

TABLE 3—A COMPARISON OF COMPOUNDS AND ELEMENTS

Compounds	Mixtures
Definite composition.	Composition in any proportion.
In preparation, heat or light emitted or absorbed.	In preparation, no evidence of light or heat.
Can only be decomposed by chemical means.	Can often be separated by mechanical means.
Composed of only *one* kind of molecule.	Composed of two or more different kinds of molecules.

EXERCISES

1. (a) What is a compound?
   (b) Give the common name, chemical name and formula of *ten* important compounds.
2. (a) What is meant by the term constituent?
   (b) What are the constituents of cane sugar?
3. (a) What happens to the properties of elements when they combine to form compounds?
   (b) Discuss briefly the formation of some simple compound which illustrates the answer to 3(a).
4. Write a short note on the carbon compounds, stressing their importance in everyday life.
5. (a) What is the Law of Definite Composition?
   (b) Why is it so important?
6. Discuss carefully the chief differences between compounds and mixtures.

CHAPTER VIII

THE CHEMICAL ELEMENTS—THE BUILDING STONES OF THE UNIVERSE

1. What Are Chemical Elements?

Scientists have made many experiments attempting to decompose mercury into simpler substances, but all means available to the ordinary chemist failed. In the same way, hydrogen and oxygen have never been broken down into other substances by the usual methods available to chemists. These undecomposable pure substances are known as chemical elements and they are the building stones of all materials in the universe. *An element can be defined as a pure substance which cannot be decomposed into simpler substances by ordinary chemical methods.*

It should be known, however, that while this definition is very satisfactory for all practical purposes, we have certain elements, known as radio-active elements, which decompose into other elements. Radium, discovered by Madame Curie in 1910, is a good example of a radio-active element. It disintegrates (breaks up) in a series of stages giving off the element helium, electrons (very small unit charges of negative electricity), and gamma rays (somewhat like X-rays), finally changing to lead after many years.

In recent years a new scientific tool known as the cyclotron or atom-smasher has been devised. By means of this machine certain elements have been disintegrated into simpler fragments. Thus, it is important that the phrase "by ordinary chemical methods" be included in the above definition of an element.

2. Occurrence of the Elements

A few chemical elements are found in nature uncombined with other elements. They are said to be in the free state. Gold, platinum, copper, sulphur, oxygen and nitrogen are examples of elements found in nature in the free state. Most of the elements, however, are combined with other elements in compounds. For example, the element sodium does not occur as the free element in nature, but it is found combined with the element chlorine as sodium chloride (common salt). Many elements are found in nature combined with oxygen, and many are also found combined with sulphur.

Most of the elements are solids at ordinary room temperature and pressure, and only two, bromine and mercury, are liquids under these conditions. A few elements are gases under ordinary conditions. Oxygen, hydrogen, nitrogen, helium, neon and chlorine are good examples of elements which normally exist in the gaseous state.

Scientists have discovered more than a quarter of a million different compounds, and the number of new materials increases every year due to the efforts of research chemists. All these different substances are made up of only 92 chemical elements. The elements are, indeed, the building stones of the universe.

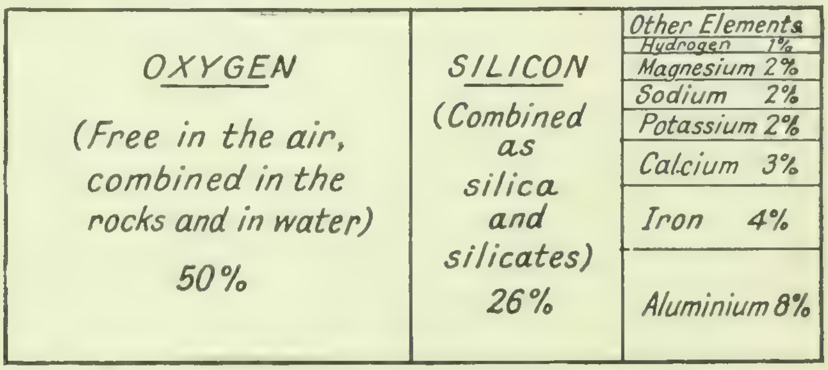


Fig. 21—The Composition of the Earth's Crust (by Weight, including the Sea and Atmosphere)

Examination of Fig. 21 shows that 98 per cent of the weight of the earth's crust, including the sea, air and living organisms, is made up of only 9 elements. These are oxygen, silicon, aluminum, iron, calcium, sodium, potassium, magnesium and hydrogen. *Oxygen* is found quite widespread in nature. It is a constituent of water and a component of the air. Oxygen is also combined with other elements to make up many of the minerals found in the earth's crust. As shown in Fig. 21 it makes up about 50 per cent of the earth's crust. *Silicon* is combined with oxygen in the common material sea sand, which is known by chemists as silicon dioxide ($Si\ O_2$). It is also present in a large class of minerals called silicates. Scientists have estimated that silicon makes up about 26 per cent of the earth's crust. *Aluminum*, the third most abundant element, is found in clay and a mineral known as *alumina* ($Al_2\ O_3$). It makes up about 8 per cent of the earth's crust. It is interesting to know that *iron*, *calcium*, *potassium*, *magnesium* and *sodium* are the only other elements present in the earth's crust in quantities exceeding one per cent. *Hydrogen*, *carbon*, *nitrogen* and all the other elements only add up to 2 per cent.

The importance of an element does not necessarily depend, however, on its abundance. For example, carbon makes up less than 0.1 per cent of the total, but without this element no life could have developed on the earth, because it is present in all organic compounds. It is rather interesting to know that the human body is made up chiefly of the four elements: carbon, hydrogen, oxygen and nitrogen. In addition, the body contains small quantities of the following elements: fluorine, sodium, magnesium, silicon, phosphorus, sulphur, chlorine, potassium, calcium, manganese, iron and iodine.

3. Symbols of the Elements

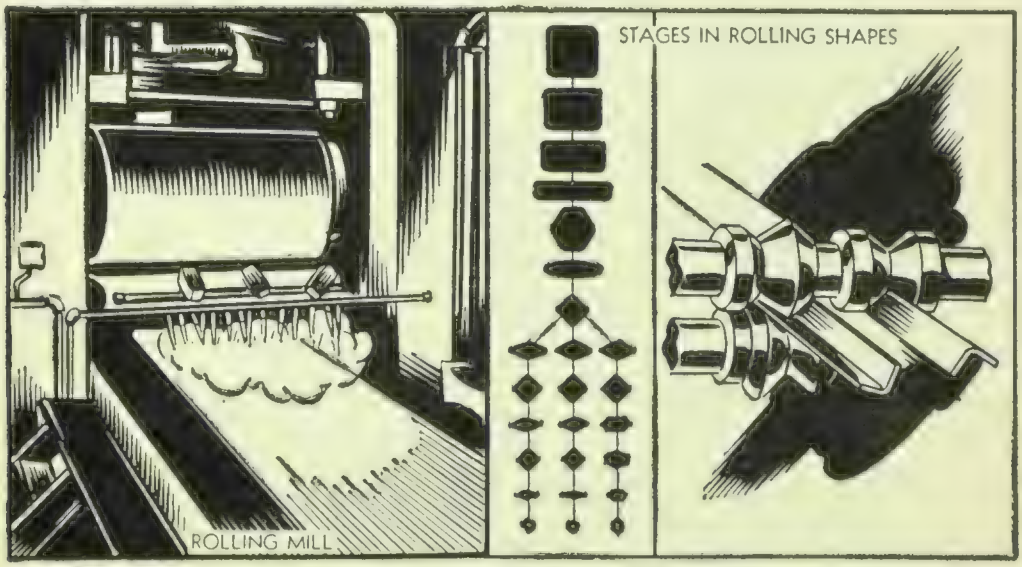
As the number and complexity of chemical compounds increased, chemists found it necessary to devise a system of abbreviations for the elements. The present system is used by chemists of all nations. Sometimes the first letter of the English name of the element was selected as the symbol and, in other cases, the first letter and one other, from the name of the element, was adopted. Sometimes the symbol was derived from the Latin name; e.g., copper, Cu from cuprum; gold, Au from aurum; iron, Fe from ferrum; lead, Pb from plumbum; potassium, K from kalium; sodium, Na from natrium; silver, Ag from argentum; tin, Sn from stannum.

Table 4—The More Imporant Elements With Their Symbols

Element	Symbol	Element	Symbol
Aluminum	Al	Manganese	Mn
Barium	Ba	Mercury	Hg
Bromine	Br	Nickel	Ni
Calcium	Ca	Nitrogen	N
Carbon	C	Oxygen	O
Chlorine	Cl	Phosphorus	P
Chromium	Cr	Platinum	Pt
Copper	Cu	Potassium	K
Fluorine	F	Radium	Ra
Gold	Au	Silicon	Si
Helium	He	Silver	Ag
Hydrogen	H	Sodium	Na
Iodine	I	Sulphur	S
Iron	Fe	Tin	Sn
Lead	Pb	Tungsten	W
Magnesium	Mg	Zinc	Zn

4. Some Important Metals

More than a hundred years ago the chemical elements were divided into two chief classes, metals and non-metals. Metals have been used by man from earliest times. Metals possess certain characteristic physical properties which usually enable one to distinguish them readily from the non-metallic elements. All metals have a silvery lustre (brightness) except gold and copper. Metals are malleable; that is, they can be made into sheets by hammering or rolling. In ancient times, glass was made so as to be malleable, but this appears to be one of the lost arts. Metals are ductile; that is, they are capable of being drawn out into threads or wire, and they are also good conductors of heat and electricity.



Courtesy o General Motors Products of Canada, Ltd.

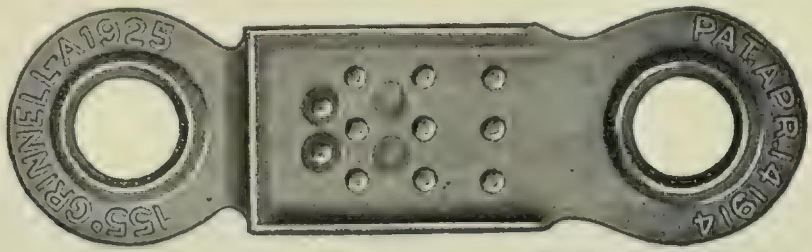
FIG. 22—A ROLLING MILL ROLLS HOT STEEL SOMETHING LIKE A ROLLING PIN ROLLS PIE CRUST

Steel sheets are being rolled in the figure at the left; L sections are being rolled at the right. The centre diagram shows the number of passes necessary to form an ingot (top) into various shapes.

The metals may be classified into light and heavy, the latter being at least five times heavier than an equal volume of water. The metals sodium and potassium are light enough to float upon water; and magnesium and aluminum are used to make light alloys. Aluminum is used to a considerable extent in the construction of aircraft. Of the heavy metals, gold, silver, copper, tin, lead, and iron have been known by man for centuries, because they occurred free in nature, or they were easily prepared from certain of their compounds called ores.

5. Alloys

Metals play such an important part in our modern civilization that it is difficult to realize what life must have been like without them. Metals are generally used in the form of an alloy. Alloys are commonly obtained by melting together certain metals. Thus *bronze*, an alloy of copper and tin, was of the highest importance to the ancients, the Bronze Age following the Stone Age.

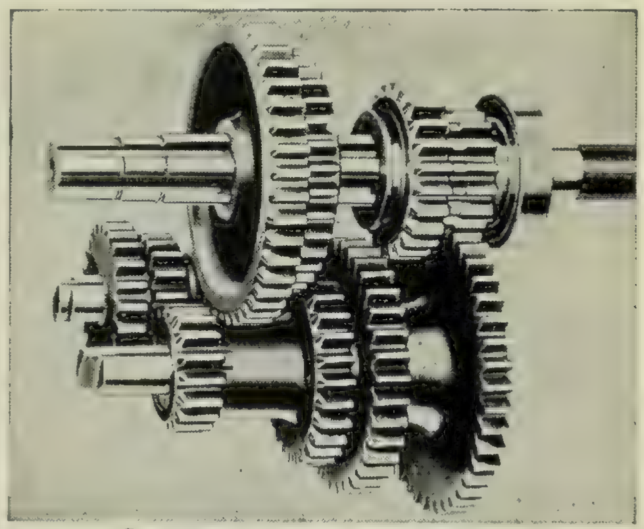


Courtesy of Grinnell Co. of Canada Ltd.

FIG. 23—A FUSIBLE LINK

Such as is used for the automatic release of fire doors. The interlocking bronze plates are soldered together with a low melting point alloy.

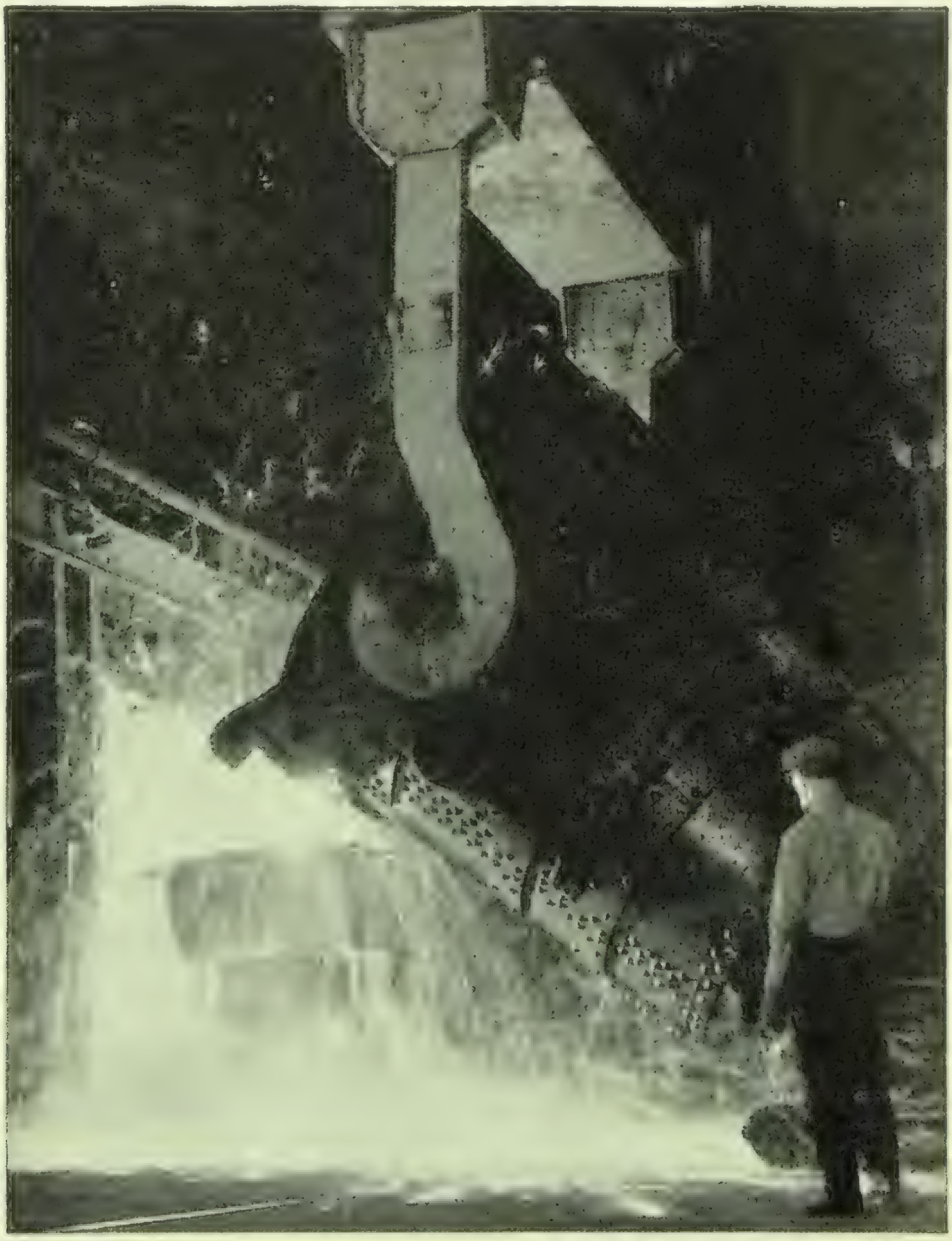
The addition of a foreign metal increases the hardness, lowers the melting point, and also lowers the conductivity for heat and electricity. Bronze, for example, possesses great fluidity when melted, and it is especially suitable for sharp and delicate castings. The ancient Egyptians, Assyrians and Greeks knew how to temper bronze, and so it was fashioned into various implements, such as knives. swords, hammers, daggers, and arrow-heads. Bronze was also used by the ancients in making splendid works of art. In modern times, *brass*, an alloy of copper and zinc has been much used instead of bronze, since it is cheaper.



Courtesy of Ford Motor Car Co. of Canada

FIG. 24—THESE AUTOMOBILE GEARS ARE MADE OF CHROME STEEL, TO ENSURE HARDNESS AND RESISTANCE TO WEAR

The engineering importance of alloys could hardly be exaggerated. Alloys are noted for the ease with which they can be shaped into various objects of superior strength by casting, rolling, forging, welding or machining. The alloys of iron, known as steels, are superior in strength and relatively low in cost; but they are heavy and rust readily. Steel is so important in our modern civilization that we often refer to our times as the Steel Age. Where the weight is a disadvantage, alloys of aluminum and magnesium are used; and where resistance to rusting is required, the copper alloys find use. In recent years the stainless steel alloys have been put to many important uses. The chief stainless steel alloy is known as "18-8" as it contains 18 per cent of the metal chromium and 8 per cent of the metal nickel.



Courtesy of Ford Motor Car Co. of Canada

Fig. 25—Pouring Steel for Automobiles

Tin plate is manufactured by dipping cleaned sheets of low carbon steel or iron into molten tin. The coating of tin prevents or retards corrosion. The resistance of the tin can to corrosion by the oxygen of the air and also to attack by the organic acids of foods is of the highest importance, because modern life is greatly dependent upon it.

6. Some Important Non-Metals

The non-metals are, as a rule, less familiar to the average person than the metals. Some of the non-metals play a very important part in our lives. Thus, oxygen is needed by the body from the time of birth until death. Carbon, in the form of coal, is used to heat our houses, or as a source of power to drive a mighty locomotive. The non-metals can be classified into gases and solids. The most important gaseous elements are oxygen, hydrogen and nitrogen. Carbon and sulphur are excellent examples of important non-metallic solid elements. The non-metals are important chiefly as raw materials from which very useful compounds can be made. For example, carbon combines with oxygen in nature to produce a colourless gas, known as carbon dioxide. This gas is an essential food for all green plants and without it all life on the earth would stop. Hydrogen and nitrogen are made to combine together by man to form a gas with a pungent odour, called ammonia. From this gas a liquid, nitric acid, can be produced by industrial chemists. Nitric acid is one of the important raw materials required to manufacture explosives and chemical fertilizers. These few examples show the important role of non-metals in our lives.

The above discussion is summarized by means of the following word equations.

Carbon + Oxygen ⟶ Carbon Dioxide
Carbon Dioxide ⟶ Plants ⟶ Foods + Fuels
Nitrogen + Hydrogen ⟶ Ammonia
Ammonia + Oxygen ⟶ Nitric Acid ⟶ Fertilizers + Explosives

EXERCISES

1. What element have water and mercuric oxide in common?
2. How could you prove that sugar contains the element carbon?
3. Classify the following as elements, compounds, or mixtures: salt, lemonade, aluminum, sugar, quicksilver, brass, steel and soil.
4. What properties are common to metals?

5. Name three metals which have a high density. Name three having a low density.
6. Name two elements that together make up about three fourths of the earth's crust.
7. Why are alloys so useful? Name three.
8. Write the names and symbols of ten important elements.
9. Name four important non-metals and tell why they are so important.
10. Write out a clear definition of the following terms: pure substance, mixture, compound, element.

CHAPTER IX

THE LANGUAGE OF CHEMISTRY

1. Molecules

Scientists believe that all matter is composed of very small invisible particles called *molecules*. The characteristics of molecules were discussed in Chapter Two. *A molecule can be defined as the smallest particle of a substance which can exist alone and have the properties of that substance.*

2. Atoms

The molecules, in turn, are composed of still smaller particles called atoms. For example, a molecule of water is composed of two atoms of hydrogen and one atom of oxygen. A molecule of hydrogen always contains two atoms of hydrogen, and a molecule of oxygen, likewise, has two atoms of oxygen. Some substances, like copper or mercury, have only one atom per molecule.

All the atoms of a given element are exactly alike in *size* and *weight*, but differ in those respects from the atoms of every other element. Atoms can combine with other atoms, and they are held together by a force called *chemical affinity*. It is this union of the atoms which produces chemical compounds. For example, two atoms of hydrogen combine with one atom of oxygen to form one molecule of water. *An atom can be defined as the smallest particle of an element which can take part in a chemical change.*

3. Chemical Symbols

It has already been pointed out that the various chemical elements are represented by symbols, some of which are given in the table on page 35. These symbols are not used as mere shorthand signs, but each one stands for *an atom* of the element. Thus, the symbol O stands for one atom of oxygen, and the symbols H, N, Na, Fe, C, represent one atom of hydrogen, nitrogen, sodium, iron and carbon, respectively, and not these substances in general. More exactly then, they are *atomic symbols*, and not merely abbreviations of the names of the elements.

4. Chemical Formulas

Molecules of a substance are produced by the combination of atoms, and so they are represented by formulas, formed by the proper combination of certain symbols. A small number placed after a symbol, just below it, gives us the number of atoms of that element in the molecule. For example, H_2 stands for a molecule of hydrogen, containing two atoms per molecule. H_2O stands for a molecule of water, which is composed of two atoms of hydrogen and one atom of oxygen.

SO_2 represents a molecule of sulphur dioxide.

FeS stands for a molecule of iron sulphide.

H_2SO_4 is the formula for a molecule of sulphuric acid.

When a large number is placed in front of a formula, it tells us the number of molecules under consideration. The following examples may help to make this fact clear.

$2\ O_2$ means that we are considering 2 molecules of oxygen, each molecule containing two atoms of this element.

2 Fe stands for 2 molecules of iron, each molecule of iron containing 1 atom. (The molecule and the atom are the same in the case of most metals.)

$5\ H_2O$ represents 5 molecules of water.

Often it is necessary to indicate a *group of atoms in a molecule which behaves like a single atom.* Such groups are known as *radicals*, and if we have more than one in a molecule of a substance, a bracket, followed by a small number to tell us the number of times the radical is taken, is placed around the radical. Several examples are given below.

Calcium hydroxide (lime-water)	$Ca(OH)_2$
Zinc nitrate	$Zn(NO_3)_2$
Ammonium carbonate	$(NH_4)_2CO_3$

5. Chemical Equations

Chemical reactions are expressed by means of equations, using an arrow instead of an equality sign. The arrow indicates the direction in which the reaction proceeds.

Equations show the way in which atoms rearrange themselves during a chemical change. According to the Law of Conservation of Mass, matter cannot be created or destroyed; therefore, equations must always have the same number of atoms on both sides.

A few of the reactions which have already been discussed may be represented by the following equations:

$$2\ HgO \longrightarrow 2\ Hg + O_2$$

The above equation represents the decomposition of mercuric oxide by heat. It shows that two molecules of this compound are needed to produce the smallest particle of oxygen which can exist alone in the free state, the molecule, O_2. It also tells us that each time an oxygen molecule is formed, two molecules of mercury, each containing one atom per molecule, are also given off.

$$2\ H_2O \longrightarrow 2\ H_2 + O_2$$

The above equation represents the decomposition of water by electrolysis. In order to make both sides of the equation balance, we must take two molecules of water, and so we secure two molecules of hydrogen and one molecule of oxygen on the right hand side of the equation.

$$2\ Na + Cl_2 \longrightarrow 2\ NaCl$$

Two molecules of sodium (containing one atom each), combine with one molecule of chlorine (containing two atoms) to produce two molecules of sodium chloride.

6. Atomic and Molecular Weights

As a result of many experiments, the consideration of which is beyond the scope of this book, the relative weights of all the elements have been determined. The standard selected for this work is the atomic weight of oxygen, which is arbitrarily set at a value of 16. Thus, *the atomic weight of an element is the relative weight of an atom of the element when compared with the weight of an atom of oxygen, selected as 16.* The atomic weights of some of the more important elements are given on the inside cover of the book.

The sum of the atomic weights of the elements in a compound gives the *molecular weight* of that compound.

7. Simple Calculations Using Formulas

Formulas can be used to help us calculate:

(1) The percentage composition of a compound.

(2) The weights of the substances which take part in a reaction.

(3) The weights of the products formed in a reaction.

In order to do these calculations the following information is necessary:

(1) Atomic weights of the elements. (See inside cover of the book.)

(2) The correct formulas of the substances involved.

(3) The *balanced* equation for the reaction under consideration.

Example 1. *To find the Percentage Composition of Water.*

The formula for water is H_2O.

The atomic weight of hydrogen (H) = 1.008; oxygen (O) = 16.00.

From the above information the molecular weight of H_2O can be calculated as follows:

$$H_2O = 2 \times 1.008 + 16.00 = 2.016 + 16.00 = 18.016$$

$$\% \text{ of Hydrogen in } H_2O = \frac{2.016}{18.016} \times 100 = 11.12$$

$$\% \text{ of Oxygen in } H_2O = \frac{16.00}{18.016} \times 100 = \frac{88.88}{100.00}$$

Example 2. *The Burning of Magnesium.*

The equation for this reaction is as follows:

$$2\ Mg + O_2 \longrightarrow 2\ MgO$$

Atomic weight of Magnesium = 24.32; Oxygen = 16.00.

By substituting these values in the equation we find that $2 \times 24.32 = 48.64$ grams (or ounces, or pounds, or tons) of magnesium combine with $2 \times 16.00 = 32.00$ grams (or ounces, or pounds, or tons) of oxygen and produce $2 \times (24.32 + 16.00) = 80.64$ grams (or ounces, or pounds, or tons) of magnesium oxide. From the above information we can calculate the amount of magnesium oxide obtained by burning any given amount of magnesium in air. Thus, a typical problem would be to calculate how much magnesium oxide could be secured by burning 5 grams of magnesium in air. This problem could be solved as follows:

$$48.64 \text{ grams of Mg} \longrightarrow 80.64 \text{ g. of MgO}$$

$$1 \text{ gram of Mg} \longrightarrow \frac{80.64}{48.64} \text{ g. of MgO}$$

$$5 \text{ grams of Mg} \longrightarrow \frac{80.64}{48.64} \times 5 = 8.30 \text{ g. of MgO}$$

EXERCISES

1. (a) What is a molecule?
   (b) Name *three* characteristics of molecules.
2. (a) What is an atom?
   (b) What is chemical affinity?
   (c) Name *two* characteristics of atoms.
3. (a) What does a symbol represent?
   (b) What is the system of selecting a symbol?
4. (a) What does a formula represent?
   (b) What is a radical? Give two examples.
   (c) Write the formulas for the following:
   oxygen, hydrogen, water, nitrogen, mercuric oxide, lime-water, hydrochloric acid, sulphuric acid.
5. Find the percentage composition of limestone ($CaCO_3$).
6. How many grams of mercury could be obtained by decomposing 10 grams of mercuric oxide completely?
7. Find the percentage composition of sand (SiO_2).
8. Find the percentage composition of common salt (NaCl).
9. How many grams of hydrogen and oxygen could be obtained by the complete electrolysis of 7.2 grams of water?
10. How many grams of oxygen could be obtained by decomposing 100 grams of mercuric oxide completely?
11. Find the percentage composition of lime-water, $Ca(OH)_2$.
12. Find the percentage composition of alumina (Al_2O_3).
13. The formula of bluestone is $CuSO_4.5H_2O$. Calculate the molecular weight of this compound.
14. How many grams of magnesium oxide could be obtained by burning 20 grams of magnesium ribbon in air?

CHAPTER X

OXYGEN

1. Introduction

It was found in Chapter VIII that oxygen is the most abundant of all the chemical elements and it is also, perhaps, the most important of the elements. For these reasons oxygen will now be studied in detail. In studying any element or compound, chemists usually employ the following outline:

(1) The importance of the element and its compounds;
(2) The occurrence;
(3) The methods of preparation;
(4) The physical properties;
(5) The chemical properties;
(6) The uses.

This method of study will be applied to oxygen and to all other elements or compounds considered in this book.

2. Importance of Oxygen

It has been known for centuries that the air contains at least two components, an active one and an inactive one. More than a thousand years ago the Chinese called the active component *yin* (oxygen). They knew that this active gas combined with sulphur, with charcoal, and with some of the metals.

Oxygen, then, is the active component of the air, of which it constitutes about one-fifth by volume. In the free state it is exceedingly abundant and widely distributed. Although oxygen is an odourless, colourless, tasteless gas, we should soon suffocate if deprived of it. We are dependent upon oxygen for heat, light and even life itself. We could not make a fire without it, and the gas is consumed in every breath we take, from the moment of birth until the heart finally ceases to beat. Among gases it occupies the supreme place of importance.

3. Occurrence

Oxygen not only occurs in the free state but it is found most abundantly in the combined state, making up by weight nearly 50% of the earth's crust, about 89% of water, 65% of the human body, and a fairly large part of all plants and animals. Oxygen also makes up a very large part of such substances as saltpetre, nitric acid, limestone, potassium chlorate, oxides, brick and mortar.

4. Preparation

(1) From Liquid Air. Oxygen is prepared in industry from liquid air. A simple diagram of the apparatus used for the production of liquid air is shown in Fig. 26. The pump (P) compresses air to about 200 atmospheres (about 3000 lbs. of pressure per square in.). The compression of a gas produces heat, which is removed as the air passes through the water-cooled spiral (S). The cooled air then goes into the liquefier in which it flows through the inner of two concentric spiral coils (I). As the gas goes through this tube, it is cooled still more by air which is flowing in the opposite direction through the outer spiral tube (O). It then escapes through the expansion valve (V) into a space where the pressure is much less, and in doing so it cools itself. The cold air is then carried back through the outer spiral (O), thus cooling the compressed gas in the inner tube (I), which is just ready to enter the chamber through the expansion valve (V). The air finally returns to the pump (P), where it is compressed, cooled, and allowed to expand through the valve, being cooled still more. The process is continued until at about −190° C. the air changes to the liquid state.

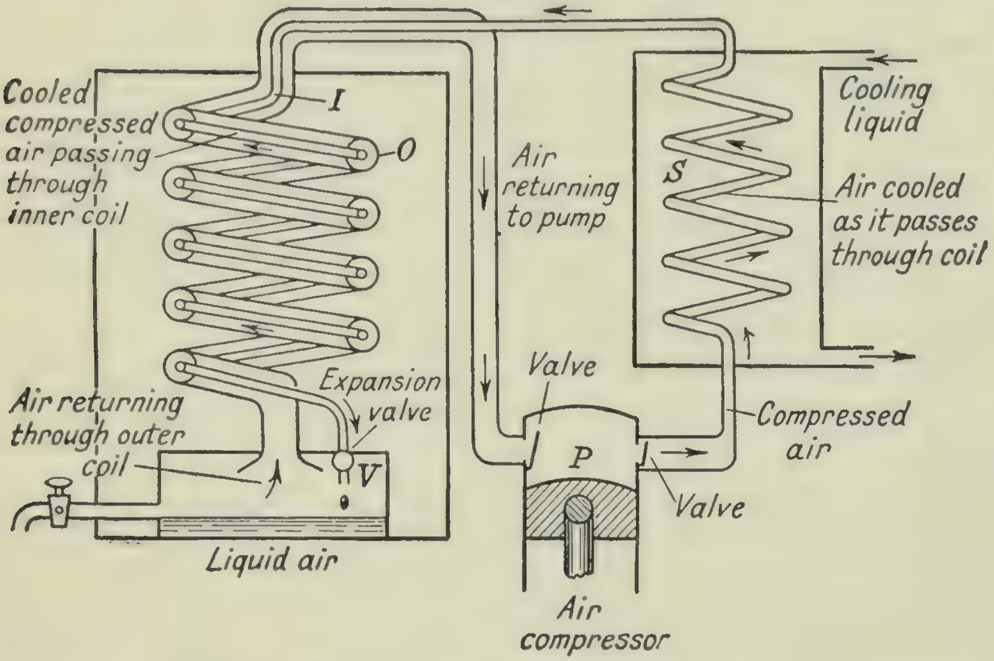

Cooled compressed air passing through inner coil
I
O
Air returning to pump
S
Cooling liquid
Air cooled as it passes through coil
Valve
Expansion valve
Air returning through outer coil
V
P
Compressed air
Valve
Liquid air
Air compressor

Fig. 26—The Manufacture of Liquid Air

Liquid air is a mixture of liquid oxygen and liquid nitrogen. The boiling point of liquid oxygen is −183° C., and that of liquid nitrogen is −196° C. Although these boiling points are only 13° C. apart the two elements can be completely separated by a process known as *fractional distillation.* This method of separating two volatile liquids can be compared to the sifting of a pile of gravel. In the case of the gravel the coarse stones can be separated from the smaller pieces by means of a suitable screen. To separate the liquid oxygen molecules from the liquid nitrogen molecules we simply add energy in the form of heat. Since the nitrogen molecules are more volatile than the oxygen molecules, we find that *nitrogen* comes off first when liquid air evaporates. Of course, the nitrogen carries away some oxygen, and it is only by means of a long *fractionating column* that almost complete separation of the two elements can be brought about. Practically pure nitrogen escapes from the top of the column, and almost pure oxygen is left behind in the distilling apparatus. The liquid oxygen is allowed to boil and it is compressed into steel cylinders for commercial use. Most oxygen produced for industrial purposes is also suitable for human consumption, as it is purer than 99 per cent, which is specified for medical purposes.

Fractional distillation is used to a considerable extent in various industries. For example, the alcohol industry uses this method to separate alcohol from certain other liquids, which are produced in the fermentation process. In the petroleum industry much of the gasoline is produced by the fractional distillation of crude oil.

(2) ELECTROLYSIS OF WATER. The decomposition of water by the electric current has already been considered, and this method of producing oxygen and hydrogen commercially is only used where electricity is inexpensive.

$$\underset{\text{water}}{2\,H_2O} \longrightarrow \underset{\substack{\text{hydrogen}\\ \text{2 vols.}}}{2\,H_2\uparrow} + \underset{\substack{\text{oxygen}\\ \text{1 vol.}}}{O_2\uparrow}$$

(3) BY HEATING MERCURIC OXIDE.

$$\underset{\substack{\text{mercuric}\\ \text{oxide}}}{2\,HgO} \longrightarrow \underset{\text{mercury}}{2\,Hg} + \underset{\text{oxygen}}{O_2\uparrow}$$

This method would not be practical for the preparation of large quantities of oxygen because mercuric oxide is expensive.

(4) BY HEATING POTASSIUM CHLORATE (usual laboratory method). In the laboratory, oxygen is usually prepared by heating a mixture of about six parts of potassium chlorate with

two parts of manganese dioxide in a pyrex test tube arranged as shown in Fig. 27.

$$\underset{\text{(potassium chlorate)}}{2\,KClO_3} \longrightarrow \underset{\text{(potassium chloride)}}{2\,KCl} + \underset{\text{(oxygen)}}{3\,O_2\uparrow}$$

The manganese dioxide undergoes no change in this process, and it is known as a *catalyst*. *A catalyst is a substance which alters the speed of a chemical reaction but it is itself unchanged.*

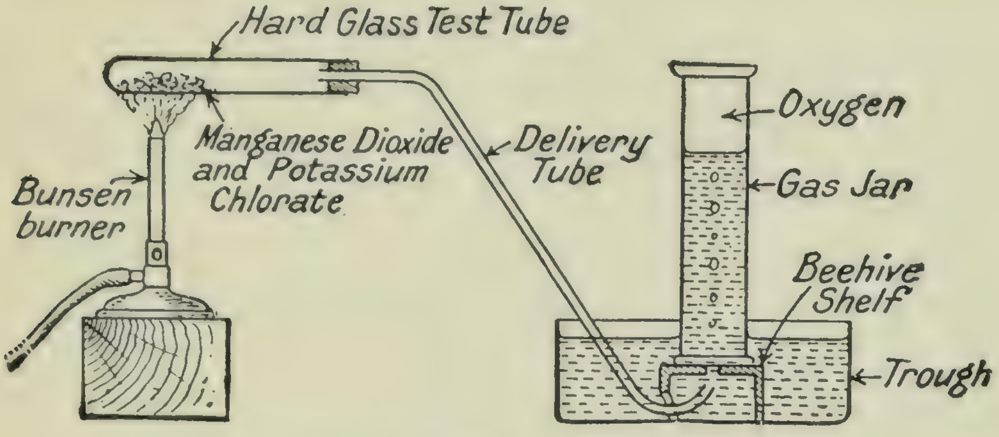


FIG. 27—MAKING OXYGEN

As a rule, a catalyst speeds up a chemical change, but there are some which retard a reaction. For example, acetanilide is added to solutions of hydrogen peroxide to slow up the decomposition of this substance.

Many processes in chemical industry are accelerated by the use of catalysts. For example, platinum is used as a catalyst in the production of sulphuric acid. Finely powdered nickel is used as a catalyst in speeding up the combination of hydrogen with certain liquid oils to produce solid fats, which are used in cooking.

Catalysts are found quite widespread in nature. The catalysts found in living organisms are known as *enzymes*, a word derived from the Greek, meaning literally "in yeast" or "in leaven". These catalysts are chemical compounds whose molecules are very complicated in structure, and they appear to be responsible for many chemical reactions which take place in the living tissue. Such problems are studied in that branch of chemistry known as biochemistry.

5. Physical Properties

(1) Oxygen is a *gas* under ordinary conditions.

(2) It is *colourless*.

(3) Oxygen is *odourless.*

(4) It is *heavier than air.* One litre of oxygen weighs 1.429 grams, while the same volume of air weighs 1.293 grams.

(5) Oxygen is *very slightly soluble* in water, 100 c.c. of water dissolving only about 3 c.c. at 20° C.

The solubility of oxygen in water is in some ways its most important physical property. Fish secure oxygen for their blood from the *dissolved oxygen* in the water which passes through their gills. In the case of air-breathing animals (like man), the oxygen could not be so easily taken into the body if it did not first dissolve in the water contained in the walls of the air sacs of the lungs. Thus, the oxygen leaves the lungs to go to the blood stream in the dissolved state.

6. Chemical Properties

(1) Oxygen *supports combustion* vigorously.

(2) It *does not burn.*

(3) *It combines with a large number of other elements.* Whenever two or more substances combine to form a chemical compound, we have a type of reaction known as *combination* or *synthesis.* The combination of oxygen with other elements is usually not marked at ordinary temperatures, but at higher temperatures oxygen reacts very vigorously, usually giving off *heat* and *light.* The substances formed when the elements combine individually with oxygen are known as *oxides,* and the process is called *oxidation.* Many oxides occur in nature as valuable minerals and ores. For example, one of the chief ores of iron is the substance known by mining men as haematite, which contains a high percentage of ferric oxide, Fe_2O_3.

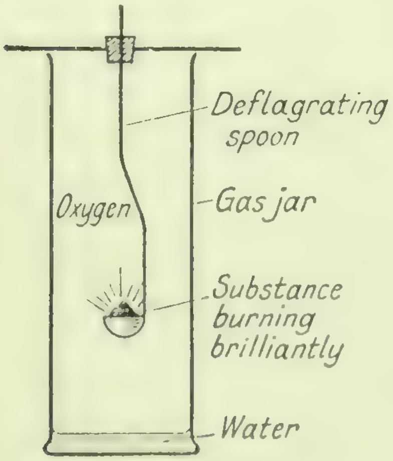


Fig. 28—Combustion in Oxygen

All familiar metals, except the noble metals (silver, gold and platinum), when heated combine with oxygen. Magnesium, for example, burns in oxygen, producing a white powder and emitting a dazzling light.

$$\underset{\text{(magnesium)}}{2\ Mg} + \underset{\text{(oxygen)}}{O_2} \longrightarrow \underset{\text{(magnesium oxide)}}{2\ MgO}$$

Calcium also burns in oxygen to produce a white substance, calcium oxide (quick lime).

$$\underset{\text{(calcium)}}{2\ Ca} + \underset{\text{(oxygen)}}{O_2} \longrightarrow \underset{\substack{\text{(calcium}\\ \text{oxide)}}}{2\ CaO}$$

Copper changes from reddish to black in colour when heated in oxygen. The black material is copper oxide.

$$\underset{\text{(copper)}}{2\ Cu} + \underset{\text{(oxygen)}}{O_2} \longrightarrow \underset{\substack{\text{(copper}\\ \text{oxide)}}}{2\ CuO}$$

It can be shown experimentally that even iron will burn brilliantly in oxygen. As the metal burns accompanied by bright sparks, it is changed into magnetic oxide of iron (Fe_3O_4), which occurs in nature as the mineral magnetite or lodestone. This oxide is exactly the same in chemical composition as the hammer-scale, which flies from the blacksmith's anvil as he hammers red-hot iron. If the air did not contain nitrogen, our steel structures would burn like wood in case they caught fire.

$$\underset{\text{(iron)}}{3\ Fe} + \underset{\text{(oxygen)}}{2\ O_2} \longrightarrow \underset{\substack{\text{(magnetic oxide}\\ \text{of iron)}}}{Fe_3O_4}$$

The oxides produced by the burning of metals in air, or oxygen, are called *basic oxides* or *basic anhydrides* because they combine with water to form a substance called a *base* or an *alkali*. The word anhydride means without water. Thus, calcium oxide or lime (CaO), formed by the burning of calcium, unites with water to form calcium hydroxide, or slaked lime.

$$\underset{\substack{\text{(calcium}\\ \text{oxide)}}}{CaO} + \underset{\text{(water)}}{HOH} \longrightarrow \underset{\substack{\text{(calcium}\\ \text{hydroxide)}}}{Ca(OH)_2}$$

A water solution of a base or alkali has a caustic taste, a slippery feeling, and turns red litmus paper to blue. A solution of calcium hydroxide is often called lime-water, and this liquid turns milky in appearance when the gas carbon dioxide is bubbled into it. It is well known to most people that when a workman adds water to lime (quicklime), the lime is changed into slaked lime, or calcium hydroxide, accompanied by much heat.

Magnesium oxide is another good example of a basic oxide and it forms magnesium hydroxide with water.

$$\underset{\substack{\text{(magnesium}\\ \text{oxide)}}}{MgO} + \underset{\text{(water)}}{HOH} \longrightarrow \underset{\substack{\text{(magnesium}\\ \text{hydroxide)}}}{Mg(OH)_2}$$

Most non-metals burn in oxygen. For example, when powdered sulphur in a deflagrating spoon is ignited and placed in oxygen, the sulphur burns vigorously with a blue flame as shown in Fig. 28.

$$S + O_2 \longrightarrow \underset{\text{(sulphur dioxide)}}{SO_2}\uparrow$$

A piece of charcoal when heated to redness continues to glow brightly in oxygen.

$$C + O_2 \longrightarrow \underset{\text{(carbon dioxide)}}{CO_2}\uparrow$$

The oxides produced by burning non-metals in oxygen are known as *acidic oxides* or *acidic anhydrides* because they combine with water to form acids. For example, carbon dioxide reacts with water to form carbonic acid.

$$\underset{\text{(carbon dioxide)}}{CO_2} + \underset{\text{(water)}}{H_2O} \longrightarrow \underset{\text{(carbonic acid)}}{H_2CO_3}$$

7. Uses of Oxygen

Oxygen is not only the most abundant element but it is the most useful, for life, heat, and light are largely dependent upon it. Considerable quantities of oxygen are used for cutting and welding metals, chiefly steel, by means of oxy-hydrogen or oxy-acetylene torches. These torches consist of two tubes, one inside the other. The hydrogen or acetylene, passing through the outer tube, and pure oxygen through the inner, mix in the correct proportions at the tip and burn with a very hot flame. Temperatures much higher than the melting point of iron are reached by the flames of these torches. Oxygen in tanks is used to restore the supply in the air of submarines.

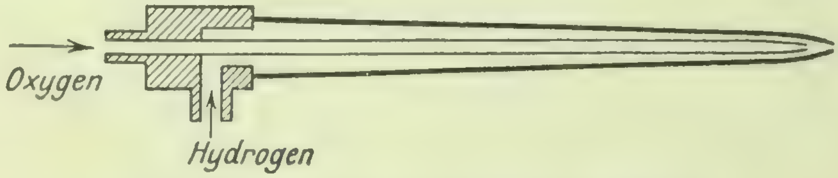


Fig. 29—An Oxy-hydrogen Blowpipe

Oxygen has several important uses in medicine. For the treatment of certain lung diseases the medical doctor uses an oxygen chamber which contains from 40 to 60 per cent pure oxygen. An inhalator giving 93 per cent oxygen and 7 per cent carbon dioxide is often used in addition to artificial respiration in cases of near drowning. Oxygen is also used to bring about recovery from electrical shock.

Oxygen is a necessity in the field of aviation. It has been found that aviators who ascend to high altitudes, such as 19,000 feet, where the air is rarefied, get only half the usual amount of oxygen and so become almost unconscious. Experience has shown that above 15,000 feet the pilot must use oxygen and it has also been found that oxygen is needed at that altitude for

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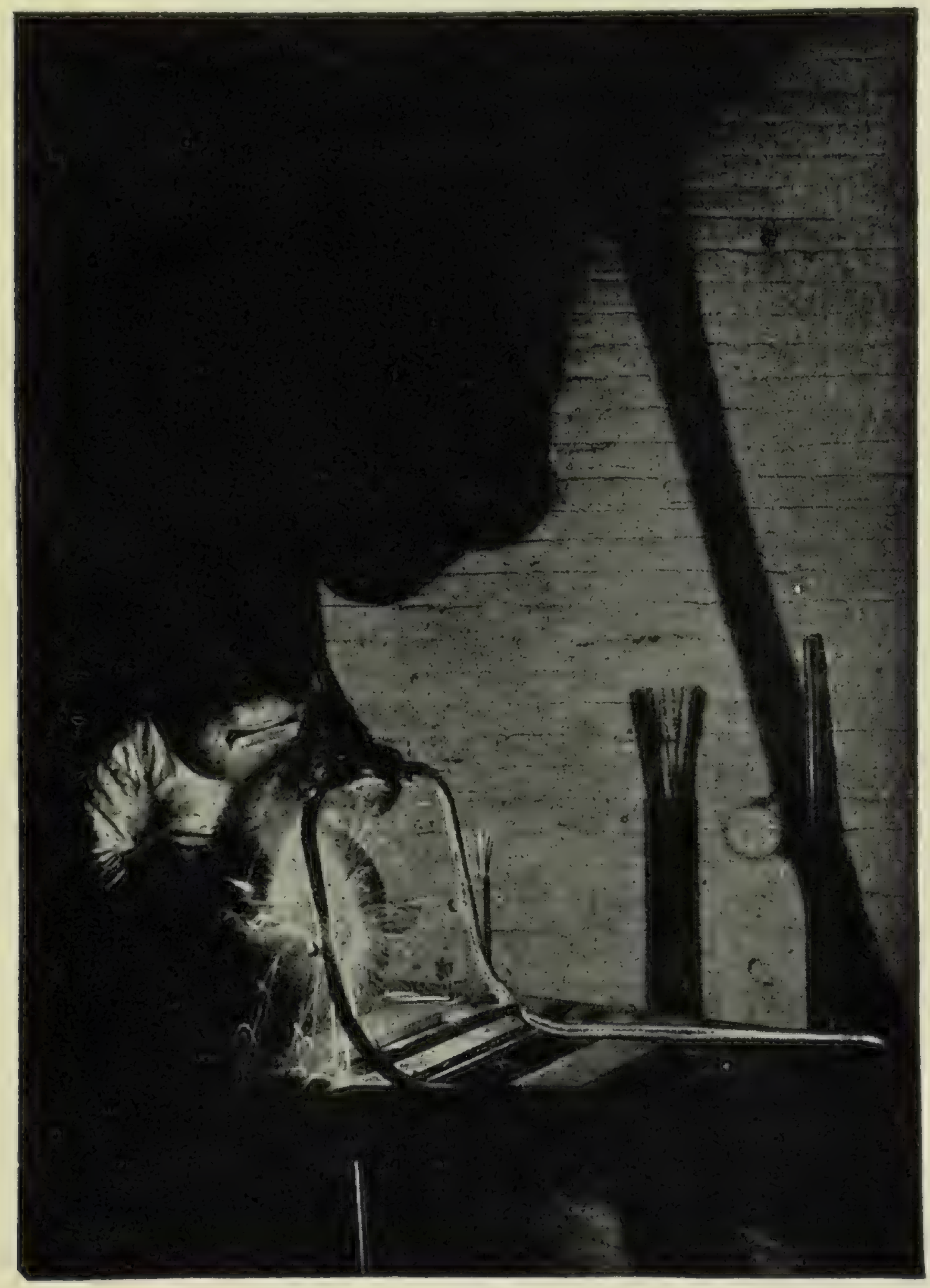


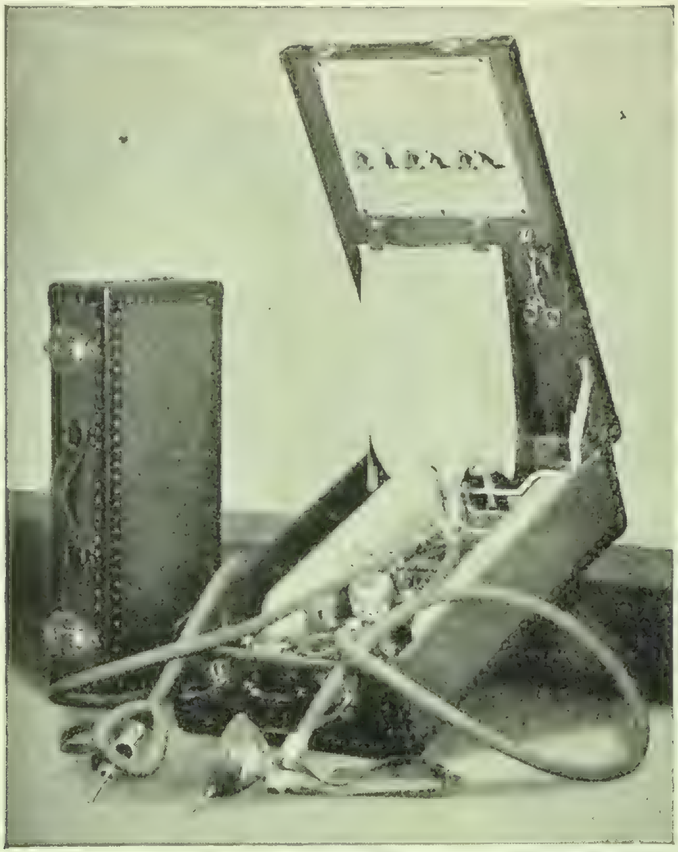
Courtesy of Lincoln Electric Co. of Canada

FIG. 30—WELDING THE FRAME OF AN AIRPLANE CHAIR

Notice the trails made by particles of burning iron.

the motors of the aircraft. This is supplied by means of the supercharger on the carburetor.

Rescue parties entering mines carry a supply of oxygen. Some of the oxygen breathing apparatus is adapted to absorb the carbon dioxide exhaled by the wearer. Experiments have shown that breathing oxygen for long intervals of time is by no means harmful.



Courtesy of LaFrance Fire Engine and Foamite, Ltd.

FIG. 31—AN INHALATOR

This device supplies the victim of carbon monoxide poisoning, electric shock, drowning, or other accident involving a cessation of breathing, with "Carbogen", a mixture of 7 per cent carbon dioxide and 93 per cent oxygen. The carbon dioxide stimulates the respiratory system, causing deep breathing, while the oxygen unites with the hemoglobin. This inhalator will allow the treatment of two patients simultaneously.

EXERCISES

(1.) (a) Where do we find oxygen in the free state?
    (b) In the combined state?

(2.) Explain how you can obtain oxygen from:
    (a) Air.
    (b) Water.
    (c) Mercuric Oxide.
    (d) Potassium Chlorate.

3. Assume that potassium chlorate is 39% oxygen. If 6 grams of potassium chlorate and 2 grams of manganese dioxide are used to produce oxygen, name the products left in the test tube and calculate how much of each remains.
4. (a) What do we mean when we say that an element such as iron is oxidized?
   (b) What name do we give to the product formed?
5. What changes take place when an element such as sulphur or magnesium burns?
6. (a) Define basic and acidic anhydrides.
   (b) Write an equation to illustrate each type of compound mentioned in (a).
7. Why do we call oxygen an element and potassium chlorate a compound?
8. (a) Can you tell from the appearance of a compound whether it contains oxygen?
   (b) Give two examples which prove your answer is correct.
9. Name two kinds of energy used in liberating oxygen from its compounds.
10. Tabulate five uses of oxygen.
11. How many grams of oxygen could be obtained by the complete decomposition of 100 grams of potassium chlorate?
12. How many grams of potassium chlorate would be required to prepare 1000 grams of oxygen?
13. A chemical engineer is required to prepare 100 tons of sulphur dioxide. How many tons of sulphur would he need?
14. A blacksmith produces 10 pounds of hammer-scale. How many pounds of oxygen were taken from the air in the formation of this weight of hammer-scale?

Chapter XI

OXIDATION

1. Introduction

In the last chapter it was found that oxygen combines readily with a large number of substances. This process is known as *oxidation* and may be defined as *the combining of a substance with oxygen.* The chief types of oxidation are:

1. Combustion or Burning.
2. Corrosion of Metals.
3. Respiration.
4. Decay.

We shall now consider each of these four kinds of oxidation in detail.

2. Combustion or Burning

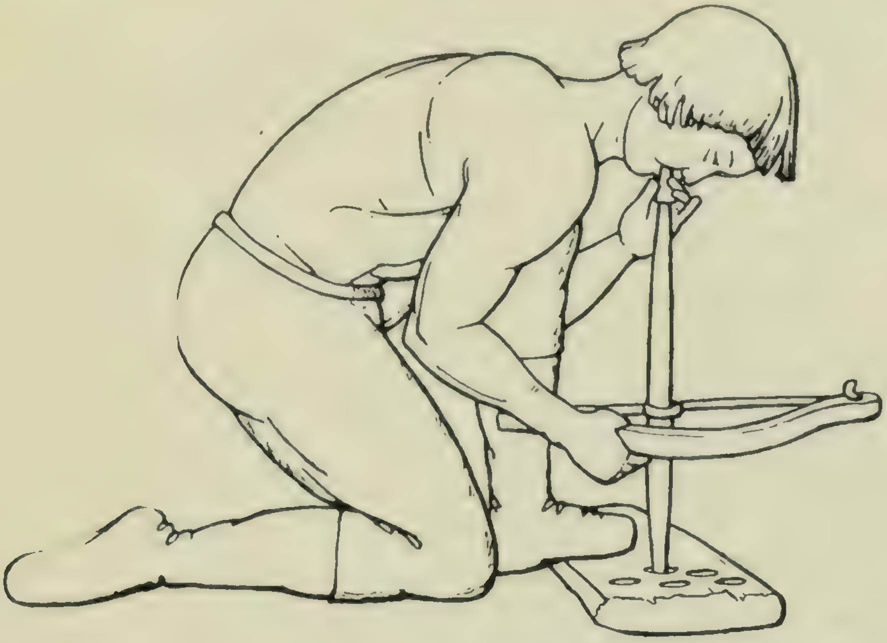
(1) *What is Combustion?* Combustion, in the popular sense, is the rapid chemical union of matter with oxygen, accompanied by the evolution of heat and light. Fire consists of heat and light produced by the rapid oxidation or combustion of fuel. However, *combustion is defined in chemistry as an act of chemical union, accompanied by the production of heat and often of light.* In most cases one of the combining substances is oxygen. We do have examples of combustion, however, in which no oxygen is involved in the reaction. The combination of powdered iron with fine sulphur to form iron sulphide,

$$\mathbf{Fe + S \longrightarrow FeS + heat + light}$$

accompanied by heat and light, is a good illustration of combustion where no oxygen is involved. Other examples which illustrate this idea will be encountered later.

(2) *Fire and Flame.* The story of fire and flame is a very interesting one. Nobody knows just when man first learned to kindle fire, but we do know that there was a time when he was unable to do so.

The ancients had some very strange ideas concerning fire and while its benefits were appreciated, its real nature was not understood. They knew that its warmth was agreeable in the winter and that it served as a guide through trackless forests. Fire was also of use to them in repelling the attacks of wild animals and for cooking their food. By means of fire, clay vessels were made suitable for use and metals were secured from certain rocks. Some ancient peoples regarded fire as a divinity and they worshipped it.



Courtesy of Royal Ontario Museum

Fig. 32—Making Fire with a Bow Drill

It may be that man first kindled fire by the *friction* of two pieces of wood. That method is still employed by the South Sea Islanders. Another ancient way of starting a fire was by striking together *flint and iron pyrites* (fire stone) in the presence of

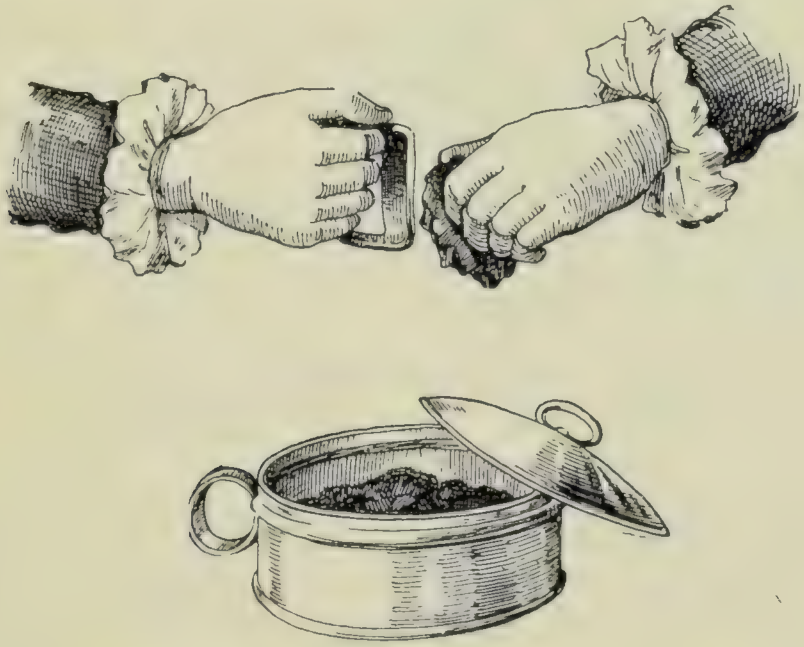


Fig. 33—Flint and Steel with Tinder Box

tinder, a method still used by certain primitive people. *Natural fires*, not kindled by man, have originated in various ways. For instance, volcanoes, earthquakes, and lightning have been responsible for starting natural fires. The *friction match* is very modern, having been invented by John Walker of England only about a century ago.

(3) *The Burning of Fuels.* From the days when man first learned to make fire until comparatively recent times, the fires of home and industry were fed only with wood. Then came the discovery of a new fuel that ushered in the *Age of Steel.* This new fuel was *coal.* The change from wood to coal revolutionized industry. The importance of coal in the smelting of iron made it the foundation upon which our modern machine civilization has been built. All the early steam locomotives and stationary engines were fired with wood. The adoption of coal for fuel gave them far greater speed. Oil has been known to man for several thousand years and it was used to some extent in all ages. Heavy oil was first used as a fuel for heating in the oil fields of Russia many years ago and it was there that the first oil burning stoves were invented. Today oil, instead of coal, is the fuel that drives the mightiest battleships and the swiftest ocean liners. Gas, obtained in nature from wells or from the heating of coal, is used to a considerable extent in both homes and industries in many parts of the world.

When a fuel burns, the chief products of combustion (in certain cases the only ones) are water and carbon dioxide. This may be shown by inverting a dry glass cylinder over a burning candle. In a short time water condenses upon the inner walls of the vessel and the addition of some clear lime-water to the cylinder proves the presence of carbon dioxide. The lime-water turns milky in appearance on shaking and this is the chemical test for carbon dioxide. The reason that the lime-water turns milky is that a fine white precipitate of calcium carbonate is formed when carbon dioxide reacts with the lime-water.

$$\underset{\text{lime-water}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\substack{\text{Calcium Carbonate} \\ \text{(insoluble)}}}{CaCO_3\downarrow} + H_2O$$

A precipitate is an insoluble substance formed when certain compounds react in solution. It is usually indicated in a chemical equation by an arrow pointing downwards. It is to be remembered that what happens when we burn a candle would also take place when other types of fuels undergo combustion.

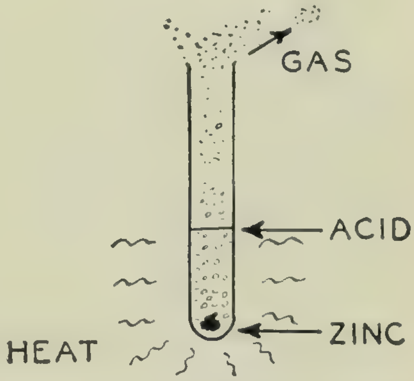
This simple experiment with a burning candle indicates that the wax, of which the candle is composed, contains the two elements hydrogen and carbon. The hydrogen combines with oxygen from the air to produce steam which condenses to water on the cold inner surface of the cylinder. The carbon combines with the oxygen of the air to produce the invisible gas carbon dioxide (CO_2). Compounds which contain only the elements carbon and hydrogen are known as hydrocarbons and they are the chief components of most fuels.

Most people burn coal to get energy in the form of heat and they are not interested in the carbon dioxide produced in the reaction.

$$\text{C (coal)} + O_2 \longrightarrow CO_2 + \text{Energy (heat)}$$

Thus, the value of a fuel lies in the amount of heat which is liberated by a unit weight. Heat is a form of energy with which we are most familiar. Light and electricity are examples of other forms of energy. It will be remembered that energy is defined in science as anything *which can do work.* It has been found by experiment that *energy may be changed from one form to another but it can never be created or destroyed.* This is known as the *Law of Conservation of Energy.*

When a chemical change takes place, energy is always given off or absorbed. In the case of the burning of fuels, energy is always given off in the form of heat and light. Reactions which give off heat are known as *exothermic* and those which absorb heat are said to be *endothermic.* The burning of charcoal and sulphur in oxygen and the action of acid on zinc are good examples of exothermic reactions. The decomposition of mercuric oxide by heat is a good illustration of an endothermic reaction.



FIG, 34—AN EXAMPLE OF AN EXOTHERMIC REACTION

$$\underset{\text{mercuric oxide}}{2\,HgO} + \textit{heat} \longrightarrow \underset{\text{mercury}}{2\,Hg} + O_2\uparrow$$

(4) A QUANTITATIVE STUDY OF COMBUSTION. It is everyday experience that when a fuel burns, it disappears more or less completely, leaving behind a small amount of ash. It would appear from this that burning consists in the breaking up of the fuel, part or all of it disappearing. This fact can be

shown by performing a simple experiment with a candle. A candle is placed on one pan of a balance and carefully balanced by means of weights or sand on the other pan. If the candle is lighted and allowed to burn for a few minutes, we observe an apparent loss in weight as the pan containing the sand drops slowly. This experiment would lend support to the *phlogiston theory* which was used for about one hundred years (1675–1775) by scientists to explain the changes taking place during combustion. According to this idea all combustible substances contained an imaginary substance called *phlogiston* combined with the ash. When a substance burned, the phlogiston escaped; so the ash would be lighter than the fuel.

Fuel = Phlogiston + Ash

The same kind of explanation was used to describe calcination (burning of metals). However, in the case of a metal, the residue left behind after the phlogiston escaped was known as the *calx* instead of the ash.

Metal = Phlogiston + Calx (oxide)

When chemists commenced to do careful quantitative experiments, they found that the weight of the calx was always greater than the weight of the metal which was heated. This discovery forced scientists to discard the phlogiston theory.

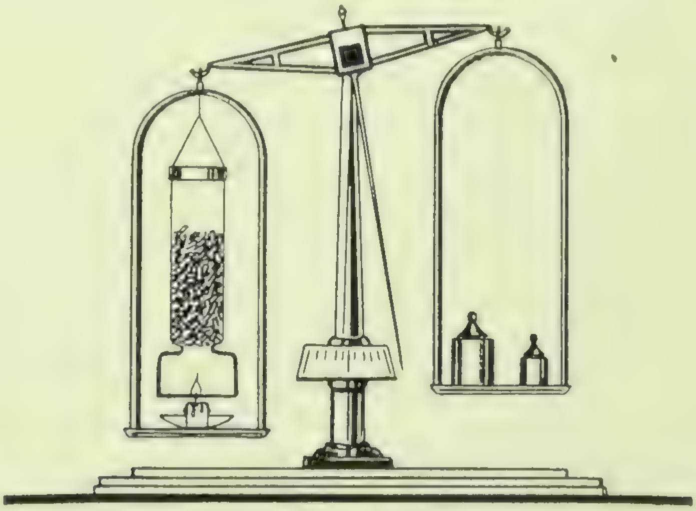


Fig. 35—Gain in Weight during the Burning of a Candle in Air

The problem which presented itself to the early chemists was to find if the burning of fuels and the calcining of metals were two different chemical processes or the same. There appeared to be a loss in weight when a fuel burns, and a gain in weight when a metal is heated in air. Most problems in chemistry can be solved by means of an experiment, and a simple experiment, again with a candle, helped to explain the above problem. A substance known as sodium hydroxide (lye) has the property of absorbing steam and carbon dioxide. If an apparatus is used, as shown in Fig. 35, it is found that there is a gain in weight when a candle is burned, just as in the case of the burning of a metal. In the case of the burning of a fuel, the products of combustion, steam and carbon dioxide, escape into the air as gases. However, when a metal is burned the product is a solid and it does not escape into the air. The true nature of combustion was discovered by the great French chemist Lavoisier, whose work was made possible when the English scientist Joseph Priestley discovered the element oxygen.

(5) THE WORK OF PRIESTLEY AND LAVOISIER. Priestley was a clergyman who delighted in doing chemical experiments in his spare time. He was especially interested in studying gases and substances which would produce gases. Some friend, knowing that Priestley liked to examine new materials, sent him a sample of a red powder, known in those days as red calx of mercury, or red precipitate. This substance is known by chemists today as mercuric oxide and every school boy, who is interested in chemistry, usually follows in the footsteps of the great Priestley by heating this material. On August 1, 1774, Priestley put some of the red calx on some mercury in an apparatus, as shown in Fig. 37, which is very different from the one used in the modern school laboratory. Priestley used a large burning glass (lens), about a foot in diameter, to focus the rays of the sun upon the red powder. By this method of heating the powder he found that a large volume of gas was given off. When Priestley thrust a burning candle into a bottle of this new gas, he was much surprised to observe that the candle burned much more brightly than in air. Priestley believed that the gas which he had discovered was "dephlogisticated air" because he was a follower of the phlogiston theory. He did not realize that he had discovered the most important of all the elements, oxygen.

Courtesy Corning Glass Works

FIG. 36

JOSEPH PRIESTLEY

Shortly after his great discovery Priestley made a trip to France, where he met Lavoisier, the most famous French chemist of that time. Priestley told Lavoisier about his experiment with red calx and the French scientist hastened to secure some of the red powder and repeat the experiment as soon as the preacher-chemist had departed. Lavoisier was a wealthy man and his laboratory was perhaps the best equipped at that time in Europe. He possessed some very delicate balances and to Lavoisier, the balance was one of the chief tools of a chemist. To show that a substance from the air was the cause of the gain in weight during the calcination of metals, and that this substance was oxygen, Lavoisier conducted the experiment which is now known as a classical piece of work. Since this is such an important experiment it is given in detail below and a diagram of his apparatus is shown in Fig. 38. The mercury in the retort was heated by means of a charcoal fire for 12 days. After this time Lavoisier made the following observations:

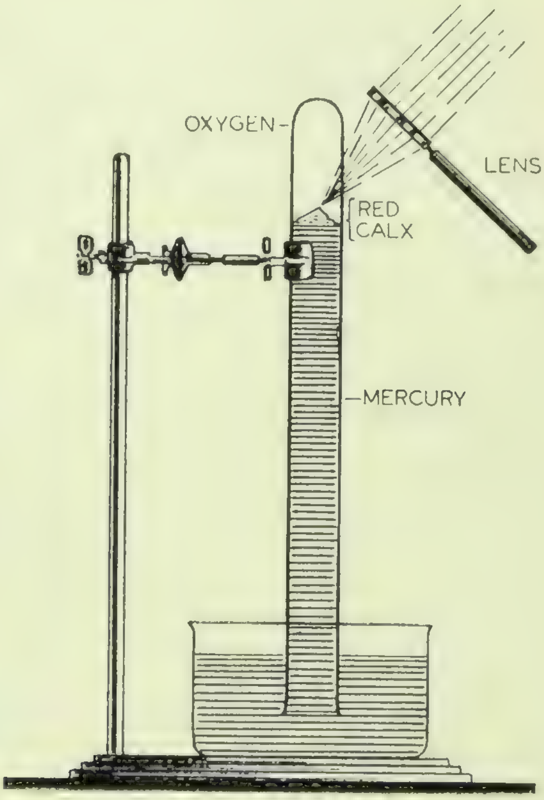
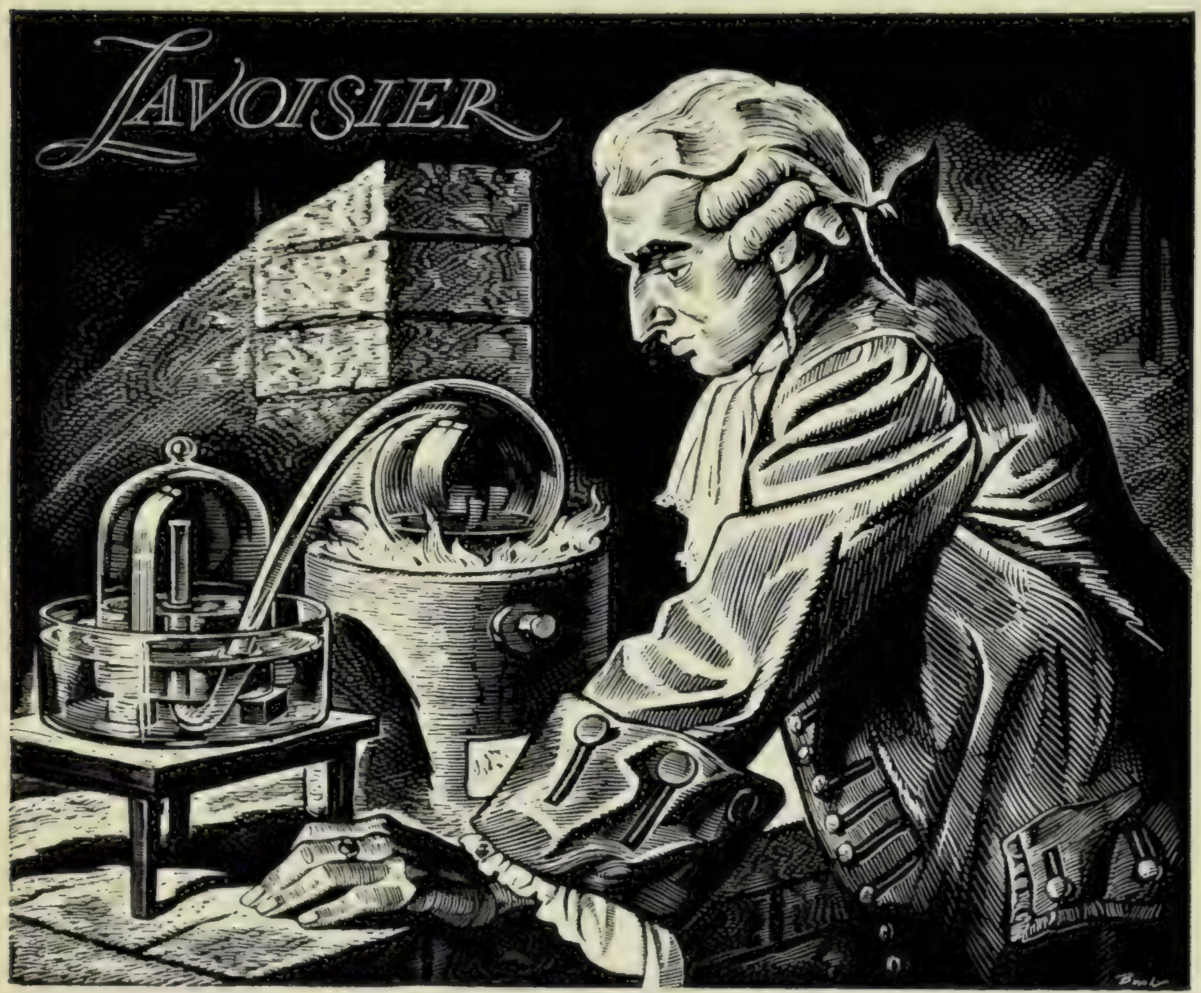


FIG. 37—PRIESTLEY'S EXPERIMENT ON RED CALX

1. *The air inside the retort and the bell-jar had lost* **one fifth** *of its volume.*

2. A lighted splint was extinguished when placed in the air which was left and it was also found that animals could not live in this gas.
3. A red powder, similar to that used by Priestley in producing oxygen, had formed on the surface of the mercury in the retort.



Courtesy of The International Nickel Company of Canada Ltd.

Fig. 38—Lavoisier (1743–1794)

The great French chemist, Antoine Laurent Lavoisier, was the founder of modern chemistry. He is shown here performing the famous experiment by which he proved the true nature of combustion. He also introduced system into the naming and grouping of chemical compounds; showed that bases and acids reacted to form salts; was an important official in the French government; and was guillotined during the French revolution because of his position in the government.

Lavoisier now placed this red powder in a suitable apparatus, heated it strongly, and collected the gas given off. He measured the volume of the gas and he discovered that it was equal to the loss in volume of the air enclosed in the retort and bell-jar.

Lavoisier's experiment proved the following facts:

1. Oxygen is a component of the air.

2. Oxygen of the atmosphere is the only gas used up in the process of combustion or burning. (Oxygen supports combustion.)
3. About one-fifth of the air by volume consists of oxygen.

Lavoisier performed many other experiments which demonstrated that combustion or burning is the combining of the fuel or metal with the oxygen of the air. He also showed that oxygen was essential for respiration. No real progress could be made in chemistry until the process of combustion was thoroughly understood and once that problem was solved the science developed very rapidly. Lavoisier also established the Law of Conservation of Mass which is a very important chemical law. For these reasons Lavoisier is often referred to as the father of modern chemistry. It was a heavy blow to the advancement of science when Lavoisier was beheaded during the French Revolution.

Since Lavoisier believed that all acids must contain this new element, which Priestley had discovered, he gave it the name of *oxygen*, which is derived from the Greek and it means "acid former." It was soon shown that this idea is incorrect, but the name of the element has remained. It should be remembered, however, that all acids do contain the element *hydrogen*. Lavoisier called the inactive component of the air *azote*, a French word which means that it cannot support life. It is now known as *nitrogen*.

(6) THE KINDLING TEMPERATURE. *The lowest temperature at which a substance will start to burn actively and continue to burn is known as its kindling temperature or temperature of ignition.*

The following conditions are necessary before a fire will start:

1. A combustible substance must be present.
2. Oxygen or some other supporter of combustion must be available.
3. The kindling temperature of the combustible substance must be reached.
4. The reacting substances must be in contact with each other.

In order to extinguish a fire the following steps must be taken:

1. The supply of oxygen (the supporter of combustion) must be cut off.
2. The fuel must be removed from the scene of the fire.
3. The temperature of the burning substance must be lowered below its kindling temperature.

Everyone knows that paper and wood will ignite more readily than coal. When we use a match to light a fire, we rub the head of the match until friction has heated it to its kindling temperature, and the tip burns. The heat of the burning tip raises the temperature of the stem to its kindling temperature. This heat elevates the paper or shavings to their kindling temperature, and so the process continues until the wood or coal reaches its kindling temperature. When such a condition is reached the coal or wood burns actively and continues to do so as long as there is plenty of oxygen and as long as the fuel lasts. Of course, as long as a fuel is cooler than its kindling temperature, it cannot burn.

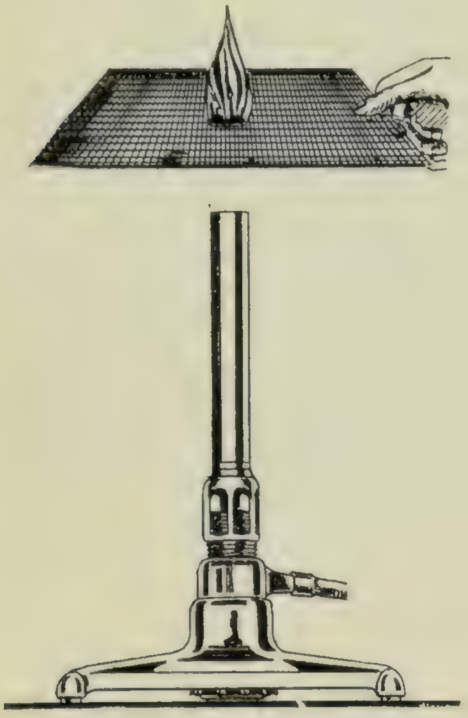


FIG. 39—AN EXPERIMENT TO ILLUSTRATE SAFETY LAMP

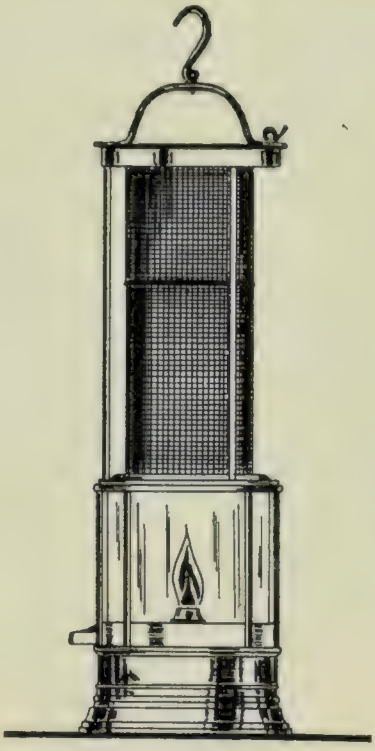


FIG. 40—DAVY'S SAFETY LAMP

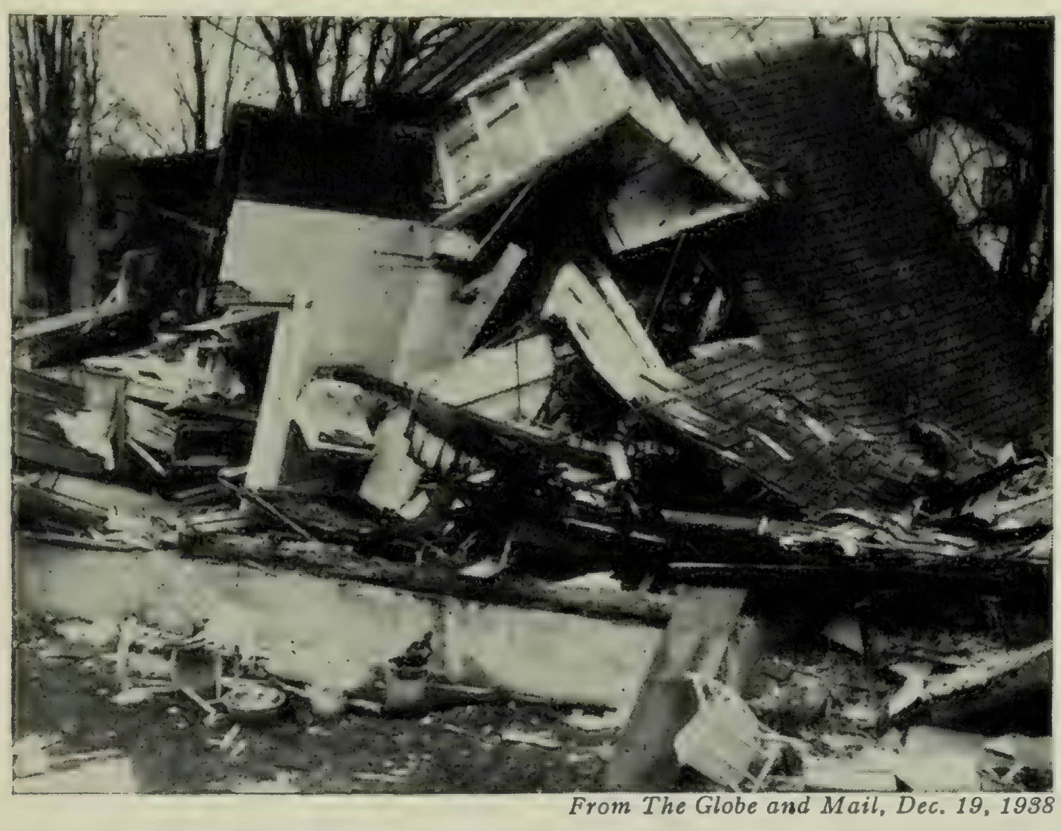
A simple experiment to illustrate kindling temperature is as follows: Ignite the gas from a Bunsen burner above an iron gauze as in Fig. 39. The gas does not catch fire below the gauze, because the iron conducts the heat away so rapidly that the kindling temperature of the gas is never reached below the wire gauge.

An important application of the above experiment was made by the great English chemist, Sir Humphrey Davy, in 1815. At that time the coal miners of England were suffering from disastrous explosions resulting from the ignition of methane (fire damp). The mine owners went to the British government to seek assistance in overcoming this serious menace to their industry. The government officials asked Davy to suggest some type of safety device. Davy with the help of Michael Faraday, who was Davy's assistant at that time, invented a miner's lamp in which the usual chimney of a lantern is replaced by wire gauze. If a miner encounters a pocket of fire damp, he is warned of its presence by small explosions taking place inside the lamp. The flame, produced by the burning wick in the miner's lamp, does not ignite the coal gas outside the lamp. This is because the wire gauze, surrounding the burning wick, conducts the heat away so rapidly that the kindling temperature of the gas is not reached outside the lamp. This invention saved the lives of many miners in all parts of the world and was named the Davy's Safety Lamp in honour of its inventor.

(7) Spontaneous Combustion. Sometimes certain slow oxidation reactions develop into a combustion which is then known as *spontaneous combustion.* To understand this, we must remember that a given weight of material, for example iron, when it combines with oxygen to form an oxide, will give out the same amount of heat whether the union proceeds rapidly or slowly. If the combination of the two materials takes place slowly, and if the heat produced escapes into the air, little rise in temperature will be observed. However, if the substance which is being oxidized is a poor conductor of heat, then we find that the heat piles up in the material until the kindling temperature is reached and active burning commences. Such a situation often arises when rags soaked with the oils used in making paint (linseed oil and turpentine) are left lying about, instead of being placed in a metal can, or better still, burned at once. These oils, in "drying," combine with the oxygen in the air, and are changed into a tough, resin-like material. As the rags are poor conductors of heat, the heat developed by the oxidation of the oils is held by the cloth instead of escaping into the air. In time enough heat is developed to set the mass on fire. Fires in coal bunkers and hay stacks arise from the same cause. The beach-wrecked carcass of the whale has been known to take fire spontaneously, due to the union of the fat with oxygen. The amount of property destroyed by fires caused by spontaneous combustion is enormous.

(8) Explosions. It is well known that when certain gases or very finely divided substances are mixed with the proper proportions of air or oxygen, they will explode if the mixture is

ignited by a spark, match, or otherwise. An explosion is due to very rapid combustion of certain gaseous mixtures, such as illuminating (coal) gas and air, hydrogen and air, acetylene and air, or very finely divided organic matter such as coal, flour, or starch, suspended in air. Certain finely divided metal dusts, such as magnesium and aluminum, as well as the dusts from some of the synthetic resins, can also form explosive dust clouds in air. It has been shown that the ignition of these explosive mixtures usually starts at one point, and the speed of explosive combustion increases rapidly.



From The Globe and Mail, Dec. 19, 1938

Fig. 41—An Open Flame was Carried Into the Cellar of This House Where Illuminating Gas had Leaked Until it Formed an Explosive Mixture With the Air

Some terrific explosions have occurred in flour mills and other factories, and because of this, modern mills have elaborate dust-removing equipment. All machinery likely to develop sparks of electricity by friction is grounded.

There are also explosions which result from the decomposition of unstable compounds such as T.N.T. (tri-nitro-toluene) and nitroglycerine.

3. The Corrosion of Metals

At ordinary temperature many substances combine slowly with the oxygen of the air. The corrosion of metals is an example of this type of oxidation. Moisture appears to be a necessary factor as well as the oxygen of the air. It has been shown that iron filings do not rust if they are placed in either dry air or in a flask of water from which the dissolved air has been driven out by boiling. Such metals as copper owe their

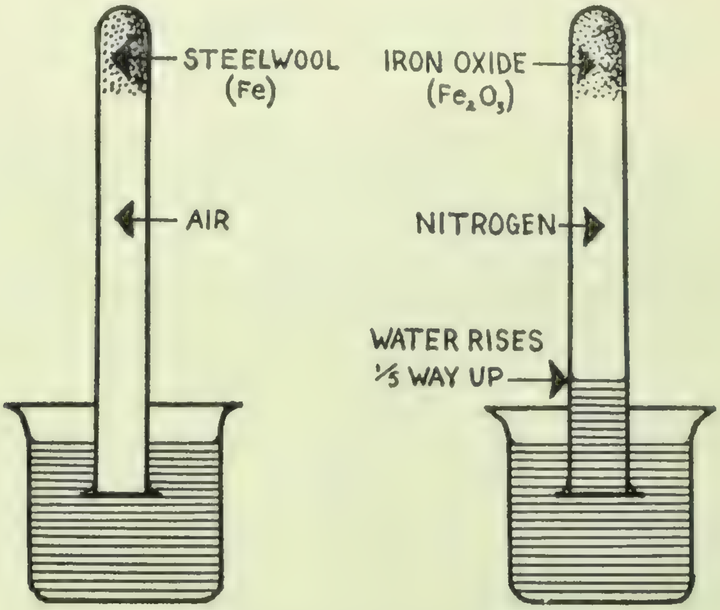


Fig. 42—Experiment to Show Nature of Rusting

Fig. 43

In a modern refinishing shop, a car on which head-lights, windows and grille-work have been masked for protection is given a new paint job by means of a spray gun.

usefulness partly to the fact that they do not oxidize even at high temperatures, and so they can be used to make articles such as kettles. The alloy brass is valuable for a similar reason.

The following experiment shows the nature of rusting. The inside of a glass tube is moistened with water and a little acetic acid which serves as a catalyst in the rusting of the iron. Some powdered iron is sprinkled into the tube so that it covers and adheres to the whole inside surface. The mouth of the tube is placed downwards in a dish of water as shown in Fig. 42. After about 30 minutes, about one-fifth of the mixture of gases confined in the tube disappears, and water rises to take its place. This experiment not only illustrates the nature of rusting, but it also shows that one-fifth of the air by volume is oxygen. Nitrogen is left in the tube.

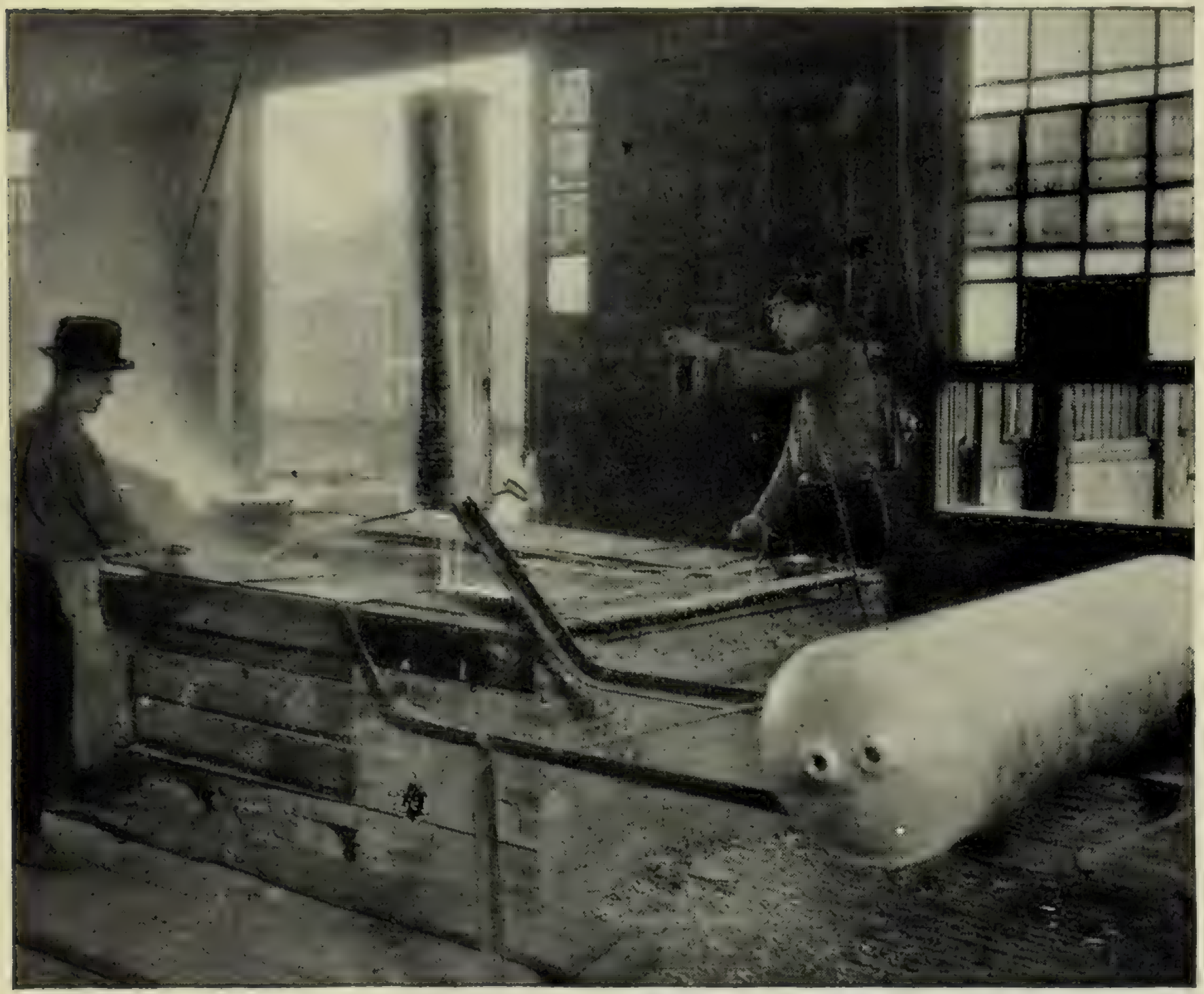

Courtesy of Canadian John Wood Mfg. Co. Ltd.

FIG. 44—GALVANIZING HOT-WATER TANKS

The formation of rust on iron and steel objects is a serious nuisance and various methods must be taken to prevent such materials from rusting. Coatings of paint, enamel, lacquer, and grease are the chief methods of preventing rust. It is an interesting fact that paints form a protective crust because they themselves oxidize in "drying."

Iron which is specially treated and which is known as *galvanized iron* is of great use in the manufacture of buckets, wire netting, shed roofs, and similar articles. The process of galvanizing consists of first treating the iron with sulphuric acid for a short time to clean the surface thoroughly and then it is dipped into molten zinc. The product made in this way has a metallic appearance and it resists attack by both moisture and oxygen. Steel may be treated in a somewhat similar way, though tin is used for the coating material instead of zinc and the product is known as *tinned plate.* The tins used to hold foods are made of sheet iron which has been subjected to a tinning process.

4. Respiration

Respiration is the term applied to the slow oxidation which takes place in the bodies of plants and animals. In the case of the human body the oxygen of the air, which is inhaled, combines in the lungs with a complex compound which is present in the red blood corpuscles. This complicated compound is known as haemoglobin and it forms with the oxygen an unstable compound called oxyhaemoglobin.

$$\textbf{Haemoglobin} + \textbf{Oxygen} \longrightarrow \textbf{Oxyhaemoglobin}$$

This unstable substance is carried from the lungs by the blood stream and it is taken to all the body cells. When oxyhaemoglobin reaches a body cell it decomposes into oxygen and haemoglobin. The oxygen combines with the carbon and hydrogen, which are present in the digested foods carried to the cell by the blood stream, to form water, carbon dioxide and most important of all, energy. It is this energy which keeps the body at its normal temperature and which supplies muscular energy. The carbon dioxide is a waste product and is carried back by the blood-serum to the lungs where it is exhaled into the air.

$$\textbf{Oxyhaemoglobin} \longrightarrow \textbf{Haemoglobin} + \textbf{Oxygen}$$

$$\underset{\text{(Carbon and hydrogen)}}{\textbf{Food}} + O_2 \longrightarrow H_2O + CO_2 + \underset{\text{(heat)}}{\textbf{Energy}}$$

5. Decay

Decay consists chiefly of slow oxidation brought about by bacteria and other organisms. It proceeds, as a rule, only when the material is moist. Dried fruits, dried leaves, and dried meat, whether dried by the sun or artificially, decay very slowly. When they are placed in a moist atmosphere, bacteria and moulds begin to grow and multiply in them, and decay sets in. The carbon and hydrogen in the decaying material are oxidized to carbon dioxide and water.

The oxygen dissolved in water is very important in the disposal of *sewage*. The sewage is mixed with large volumes of water, not only to dilute the sewage but to have it undergo oxidation by coming in contact with dissolved oxygen.

EXERCISES

1. (a) Define Oxidation.
   (b) Under what headings can we study oxidation?
2. What is combustion or burning? It is accompanied by what forms of energy?
3. (a) How did man first kindle fire?
   (b) How have natural fires originated?
   (c) Write a note on the uses and importance of coal in industry.
4. Write a note on the work of Priestley and Lavoisier.
5. Give, with the reason, each step you would take in starting a coal fire.
6. (a) What kind of combustion is said to occur when a substance takes fire without the application of external heat?
   (b) How do you account for such fires?
7. (a) What is an explosion?
   (b) What precautions do modern mills take to prevent explosions?
8. (a) What is rusting?
   (b) Is moisture necessary?
   (c) How do we prevent iron and steel objects from rusting?
   (d) What is galvanized iron?
   (e) What is tinned plate?
9. Describe briefly oxidation in the animal body.
10. Describe the part which oxygen plays in decay.
11. How many pounds of oxygen would be needed for the complete combustion of 100 pounds of charcoal?
12. A student was given 5 grams of powdered iron and told to make iron sulphide. How many grams of sulphur would be required to combine with this weight of iron?

CHAPTER XII

HYDROGEN

1. History

Many years ago the first chemists, who were known as alchemists, in their experiments with various solids and liquids, had discovered gases which could be set on fire. For example, when oil of vitriol (sulphuric acid) was poured on iron, a gas, known as "inflammable air," was produced. Sir Henry Cavendish, a great English chemist, made a special study of this gas in 1766, preparing it by the action of acids upon certain metals as well as by the action of steam upon iron. Cavendish observed that water was produced when the gas was burned in air. Lavoisier showed that this gas is an element and he named it hydrogen, from two Greek words meaning "water producer."

2. Occurrence

Hydrogen is not nearly as abundant as oxygen; moreover. it differs from oxygen in that only very small amounts of it occur on the earth in the free state. It occurs in the atmosphere in such small amounts that only a specially trained chemist can detect it. Its compounds, however, are very abundant. Hydrogen is present in water in the combined state to the extent of 11.2 per cent by weight. All acids contain this element and it is also found in the bodies of all plants and animals. Combined with carbon it forms many compounds, known as hydrocarbons, which mixed together make up petroleum (crude oil) and natural gas. Such important substances as foods and fuels of all kinds contain hydrogen. While only traces of free hydrogen occur on the earth, it is an interesting fact that the free element is present in enormous quantities in the gases surrounding the sun and certain other stars.

3. Preparation

Hydrogen can be prepared in a number of ways, the most important of which are the following:

(a) FROM WATER. Since water contains hydrogen (in the combined state) and since this liquid is so abundant, it is only natural that we should try to obtain the element from this source. It is possible to liberate the hydrogen in water in two general ways:

(1) We may use the method of electrolysis already described (page 28) and in this way obtain both hydrogen and oxygen, or

(2) we may act on water with certain metals which will combine with the oxygen of the water and liberate the hydrogen. In the case of a few of the metals this change occurs at ordinary temperatures. Thus, if a small piece of metallic sodium is dropped on water, action begins at once. The metal is lighter than water and runs hissing about on the surface of the water. We may collect the hydrogen which is evolved by the action of sodium on water as shown in Fig. 46.

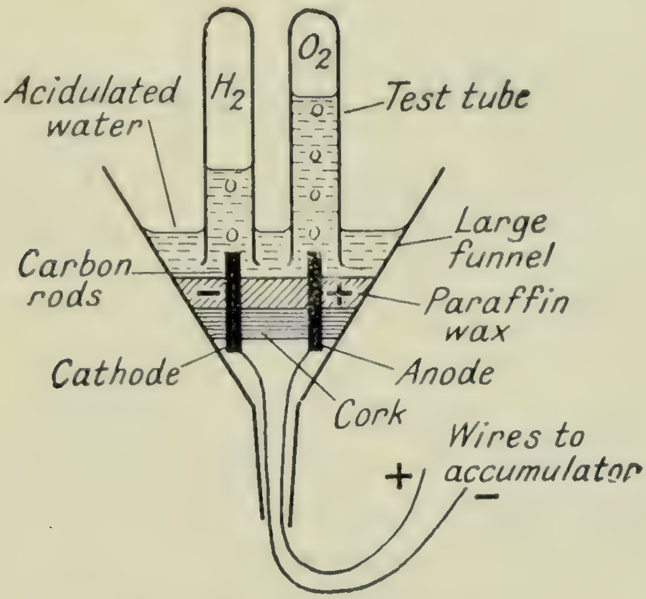


FIG. 45—THE ELECTROLYSIS OF WATER

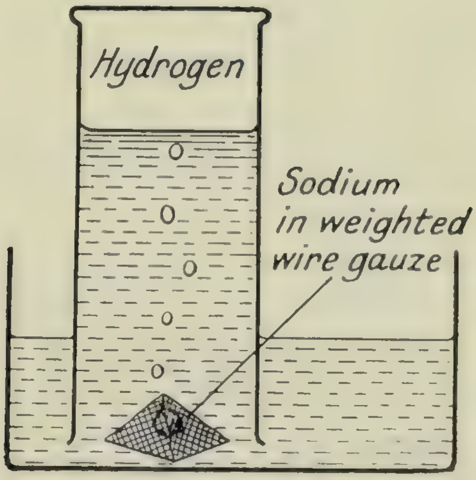


FIG. 46—THE ACTION OF SODIUM ON WATER

If potassium is used the action is more violent and so much heat is generated that the hydrogen is set on fire. When calcium is used the metal sinks to the bottom of the vessel, so that a test tube filled with water can easily be inverted over the metal to collect the gas as it is formed as shown in Fig. 47. In each of these cases the *metal displaces* only one-half of the hydrogen in the water; it combines with the remaining half and with all of the oxygen to form the compound known as the *hydroxide* of the given metal. The chemical reaction of sodium and water may be expressed thus:

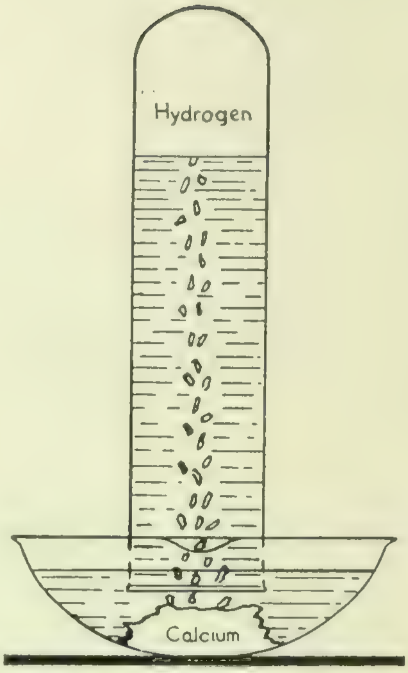


Fig. 47
Calcium on Water

$$\underset{\text{(sodium)}}{2\ \mathrm{Na}} + \underset{\text{(water)}}{2\ \mathrm{HOH}} \longrightarrow \underset{\text{(hydrogen)}}{\mathrm{H_2}\uparrow} + \underset{\text{(sodium hydroxide)}}{2\ \mathrm{NaOH}}$$

The sodium hydroxide formed remains dissolved in the excess of undecomposed water, and turns red litmus paper blue, showing that it is a *base.* By evaporating this solution to dryness we obtain the sodium hydroxide (lye) as a white solid.

The equations for the reactions of the other metals, mentioned above, with water are given below:

$$\underset{\text{(potassium)}}{2\ \mathrm{K}} + \underset{\text{(water)}}{2\ \mathrm{HOH}} \longrightarrow \underset{\text{(hydrogen)}}{\mathrm{H_2}\uparrow} + \underset{\text{(potassium hydroxide)}}{2\ \mathrm{KOH}}$$

$$\underset{\text{(calcium)}}{\mathrm{Ca}} + \underset{\text{(water)}}{2\ \mathrm{HOH}} \longrightarrow \underset{\text{(hydrogen)}}{\mathrm{H_2}\uparrow} + \underset{\substack{\text{(calcium hydroxide)}\\\text{(lime-water)}}}{\mathrm{Ca(OH)_2}}$$

Other metals, such as *iron,* decompose water rapidly but only at higher temperatures. When steam is passed over red-hot iron, the iron combines with the oxygen of the steam, forming magnetic oxide of iron and setting free all of the hydrogen as a gas. Hydrogen is sometimes prepared in this way commercially.

$$\underset{\text{(iron)}}{3\ \mathrm{Fe}} + \underset{\text{(steam)}}{4\ \mathrm{H_2O}} \longrightarrow \underset{\text{(hydrogen)}}{4\ \mathrm{H_2}\uparrow} + \underset{\text{(magnetic oxide of iron)}}{\mathrm{Fe_3O_4}}$$

In conclusion it can be said that the active metals form bases along with hydrogen when they react with water, and the less active metals produce oxides with steam in addition to hydrogen.

(b) FROM ACIDS (usual laboratory method). All acids contain hydrogen, and *certain* metals when brought in contact with them, dissolve. In the change which takes place the hydrogen of the acid is liberated. This furnishes a convenient way of preparing hydrogen in the laboratory, using the apparatus as shown in Fig. 48. It has been found by experience that the metals *zinc* or *iron* and either dilute *hydrochloric* or dilute *sulphuric* acids are the best materials to use when preparing hydrogen in the laboratory by this method. The equations for these reactions are as follows:

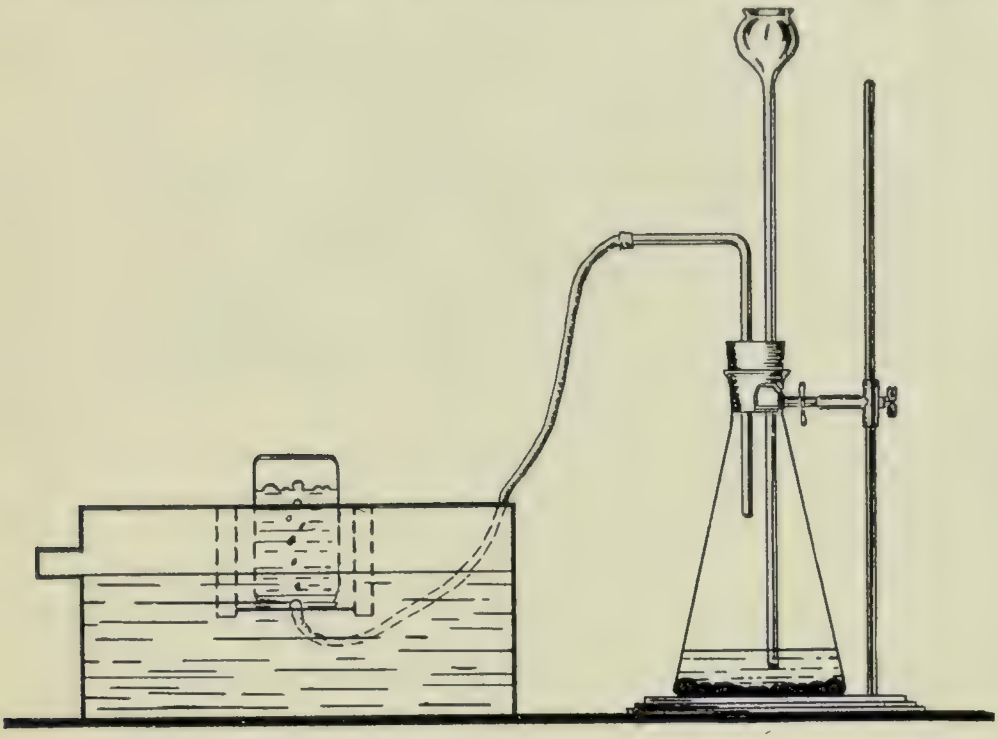


FIG. 48—LABORATORY PREPARATION OF HYDROGEN

$$\underset{\text{(Zinc)}}{Zn} + \underset{\text{(Sulphuric Acid)}}{H_2SO_4} \longrightarrow H_2\uparrow + \underset{\text{(Zinc Sulphate}}{ZnSO_4}$$

$$\underset{\text{(Zinc)}}{Zn} + \underset{\text{(Hydrochloric Acid)}}{2\,HCl} \longrightarrow H_2\uparrow + \underset{\text{(Zinc Chloride)}}{ZnCl_2}$$

$$\underset{\text{(Iron)}}{Fe} + H_2SO_4 \longrightarrow H_2\uparrow + \underset{\text{(Ferrous Sulphate)}}{FeSO_4}$$

$$Fe + 2\,HCl \longrightarrow H_2\uparrow + \underset{\text{(Ferrous Chloride)}}{FeCl_2}$$

The other products formed in the above reactions belong to a group of chemical compounds known as salts.

Examination of the above equations shows that in all cases the metal takes the place of the hydrogen in the acids, liberating the hydrogen as the free element. This kind of chemical change is called *simple replacement* or *displacement*. It is also known as *substitution.* In such reactions an element displaces one of the elements from a compound, setting it free, and unites with the rest of the constituents of the compound. Thus, in the reaction between zinc and dilute hydrochloric acid, the metal takes the place of the hydrogen, liberating it, and the zinc combines with the chlorine in the hydrochloric acid to form zinc chloride, a white solid which is soluble in water.

It was mentioned at the beginning of this discussion that *only certain metals* will react with dilute acids to produce hydrogen. Chemists have found by experiment that the metals can be arranged in a vertical table known as the *simple replacement series* or the *electromotive series.* Hydrogen, although not a metal, is one of the elements in the series and only those metals above hydrogen in the table will displace it from dilute acids. This table can also be considered as an *activity table* because the most active metals chemically are at the top and the most inactive are at the bottom.

Potassium
Sodium
Calcium
Magnesium
Aluminum
Zinc
Iron
Nickel
Tin
Lead
Hydrogen
Copper
Mercury
Silver
Platinum
Gold

The first metal on the list, potassium, displaces the hydrogen from water so violently that the gas catches fire; the second displaces it vigorously; the third less vigorously. Magnesium needs hot water and iron superheated steam. Copper and the metals following it do not liberate hydrogen from water.

It will be remembered that all the metals combine with oxygen when heated except the last three on the table. The elements just above silver do combine with pure oxygen with difficulty and the others combine with oxygen more readily as we ascend the list.

4. Physical Properties

(1) Hydrogen, like oxygen, is a *gas* under ordinary conditions.
(2) It is *colourless*.
(3) The gas is odourless.
(4) The most characteristic property of hydrogen is its *extreme lightness*, one litre of it weighing approximately 0.09 grams. An equal volume of air weighs about 14.5 times as much as hydrogen. The extreme lightness of the gas may be shown by pouring it upward from one vessel to another.
(5) Hydrogen is *very slightly soluble* in *water*, 100 c.c. of water at 20°C. dissolving 1.8 c.c. of the gas.

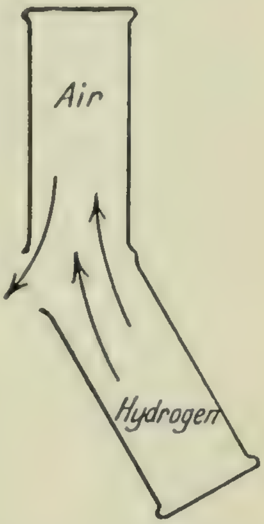


Fig. 49—Pouring Hydrogen Upwards

5. Chemical Properties

(1) At ordinary temperatures hydrogen is not an active element. At higher temperatures, however, it combines with

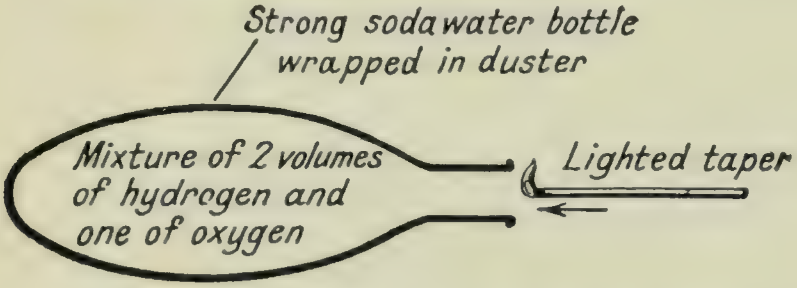

Strong soda water bottle wrapped in duster
Mixture of 2 volumes of hydrogen and one of oxygen
Lighted taper

Fig. 50—Explosion of Mixture of Oxygen and Hydrogen

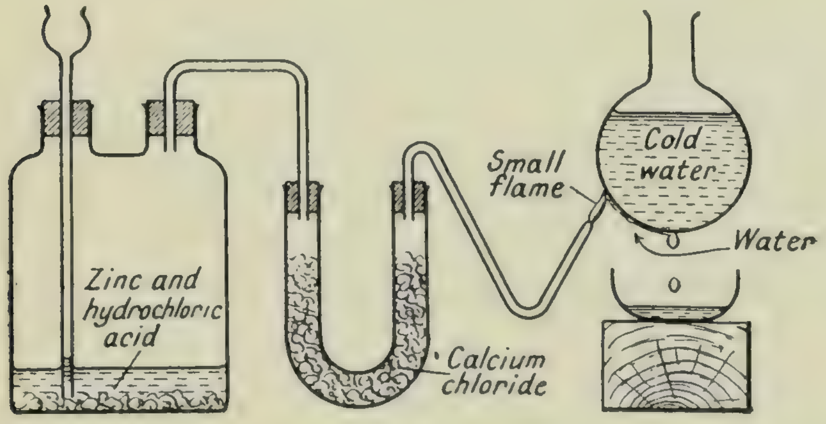


Fig. 51—Production of Water by Burning Pure Hydrogen in Air

many of the elements forming compounds, the most important of which is *water*. If we mix hydrogen and oxygen at room temperature, no action takes place. If the mixture is heated to about 800° C., or if a flame is brought in contact with it, the two gases combine with explosive violence. However, if we select the correct conditions, we can cause the two gases to combine with perfect safety. This can best be done by burning a stream of pure hydrogen in air. The combustion is due to the direct union of the hydrogen and oxygen, and the product is ordinary water.

$$\underset{\text{(hydrogen)}}{2\,H_2} + \underset{\text{(oxygen)}}{O_2} \longrightarrow \underset{\text{(water)}}{2\,H_2O}$$

(2) Although hydrogen is itself readily combustible yet it is not *a supporter of combustion;* that is, substances will not burn in it.

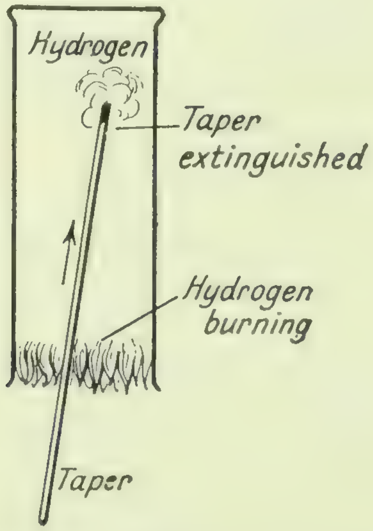


FIG. 52
HYDROGEN BURNS BUT DOES NOT SUPPORT COMBUSTION

(3) Hydrogen has the property of removing oxygen from many substances under certain conditions and this process is known as *reduction*. The material which brings this about is called a *reducing agent* and hydrogen is a good example of such a substance. For example, when *dry* hydrogen is passed over hot copper oxide, the hydrogen combines with the oxygen of the copper oxide to form water as shown in Fig. 53. The equation for this reaction is as follows:

$$\underset{\text{(copper oxide)}}{CuO} + H_2 \longrightarrow \underset{\text{(copper)}}{Cu} + H_2O$$

In this experiment the hydrogen is the *reducing agent* because it removes the oxygen from the copper oxide. The copper oxide is an *oxidizing agent* because it supplies the oxygen to form water with the hydrogen. The copper oxide is reduced to free copper and the hydrogen is oxidized to water. Reduction is always accompanied by oxidation and these two processes occur in many reactions in the bodies of plants and animals as well as in certain industries. Carbon, aluminum and carbon monoxide are other examples of reducing agents.

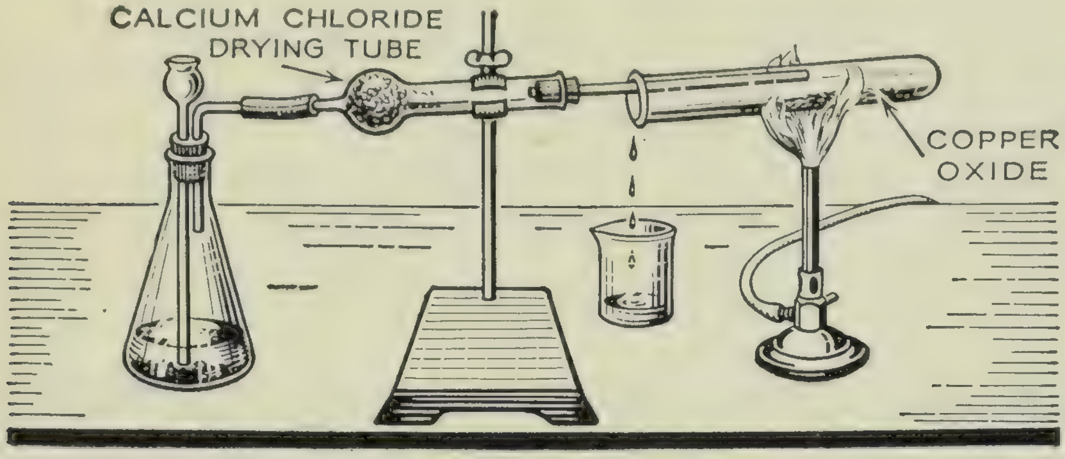


FIG. 53—REDUCING COPPER OXIDE

Reduction is thus a loss of oxygen and oxidation is a gain of oxygen. A reducing agent is a substance which removes oxygen; an oxidizing agent is a substance which gives up oxygen.

(4) *Hydrogen combines with a number of other elements* as well as with oxygen. A compound consisting of hydrogen and one other element is known as a *hydride.* Some hydrides have important uses. Ammonia, hydrogen sulphide and hydrogen chloride are examples of hydrides and the equations for their formation are shown below.

$$3\,H_2 + N_2 \longrightarrow 2\,NH_3 \text{ (ammonia)}$$
$$H_2 + S \longrightarrow H_2S \text{ (hydrogen sulphide)}$$
$$H_2 + Cl_2 \longrightarrow 2\,HCl \text{ (hydrogen chloride)}$$

6. Uses of Hydrogen

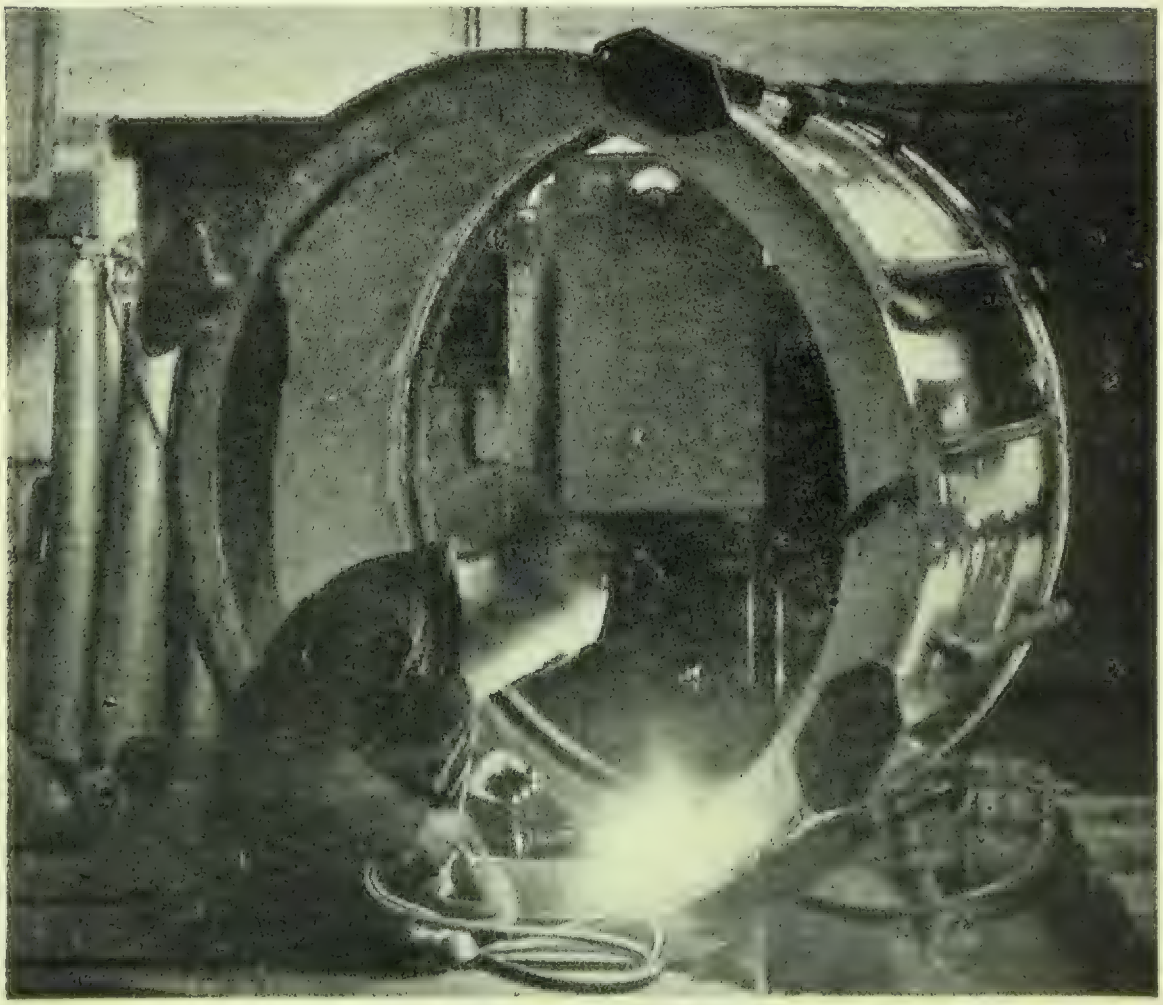
(1) Since hydrogen is the lightest gas known it is used to fill *balloons* and dirigible airships. Because hydrogen is explosive, it is replaced by helium for such purposes whenever possible. Helium, unlike hydrogen, does not burn.

(2) Much hydrogen is used *for changing certain liquid fats or oils into solid fats* used in cooking. For example, when hot cotton-seed oil is treated with hydrogen, in the presence of a catalyst such as finely divided nickel, the oil combines chemically

with the hydrogen to form a new compound, which becomes a solid fat when cooled to room temperature. Of course, the powdered nickel is removed by filtration from the reaction mixture before cooling, and the metal can be used again as a catalyst. Certain much advertised shortening materials are produced in this way, the process being known as the *hydrogenation of oils.*

(3) Hydrogen is used in the *liquefaction process* to prepare *synthetic gasoline.* This is done by subjecting a mixture of powdered coal, heavy oil and hydrogen to a pressure of about 3,000 pounds per square inch and a temperature of about 450° C. in the presence of a catalyst.

(4) Another important use of hydrogen is in the production of *ammonia* from the nitrogen of the air by the Haber Process. Ammonia can be oxidized to nitric acid, which is necessary for the manufacture of explosives.



Courtesy of The British Thomson-Houston Co. Ltd., Rugby

FIG. 54—ATOMIC HYDROGEN WELDING
The control panel may be seen in the background, and the cylinders of hydrogen on the left.

(5) Hydrogen is also used for the *synthesis of methanol* (*wood alcohol*). This is done by passing a mixture of hydrogen and carbon monoxide (CO), at about 400° C. over a catalyst.

$$CO + 2\,H_2 \longrightarrow CH_3OH \text{ (methanol)}$$

(6) The flame produced when hydrogen burns is very hot, about 2400° C., and it is particularly so if oxygen is forced into the flame in a suitable burner (see Fig. 29). This apparatus is called the oxy-hydrogen blowpipe and produces heat so intense that platinum (melting point is 1740° C.) may be readily melted. The oxy-acetylene torch has largely displaced the oxy-hydrogen blow pipe because the temperature obtained from it is much higher, about 3300° C., which is only a few hundred degrees below that of the electric furnace or arc. The oxy-acetylene flame is used a great deal for cutting and welding metals. For example, it is used for welding pipe lines and for cutting thick armour plate. It will cut through sixteen-inch metal plate quite as readily as a saw cuts wood.

Recently, an electric welding torch has been developed using hydrogen. A stream of hydrogen molecules is changed into atoms by the high temperature of an electric arc. The hydrogen atoms recombine into molecules, producing a great deal of heat in the process.

$$\underset{\text{(hydrogen atom)}}{H} + \underset{\text{(hydrogen atom)}}{H} \longrightarrow \underset{\text{(hydrogen molecule)}}{H_2} + 103{,}000 \text{ calories}$$

This heat, together with the heat produced by the burning of hydrogen molecules, gives a temperature of 4000-5000° C. and it is used in the welding of certain metals.

EXERCISES

1. Give the form (free or combined) and relative abundance of hydrogen in each of the following:
   (a) Earth's crust; (b) water; (c) earth's atmosphere; (d) sun's atmosphere.
2. (a) Who first obtained hydrogen in a pure state?
   (b) Who gave it its present name?
3. Give two general ways of preparing hydrogen from water.
4. Write the equation and name the products of the reaction of sodium on water.
5. Write the equation and name the products of the reaction of iron on steam.

6. (a) What element is present in all acids?
   (b) How can it be set free?
7. Write the equation for the usual laboratory method for preparing hydrogen. Give the names of the substances used and the products formed in the reaction.
8. Mention one very important precaution that should be taken in preparing hydrogen.
9. Compare hydrogen and oxygen as to:
   (a) weight; (b) colour; (c) odour; (d) solubility in water.
10. In the ordinary meaning of the term, should you say that hydrogen burns or that it supports combustion?
11. What two properties of hydrogen are shown by thrusting a lighted splint up into an inverted cylinder of the gas?
12. Tabulate five practical uses of hydrogen.
13. After hydrogenation, how does cotton seed oil differ in properties from the original? Has a new compound been formed?
14. What causes a balloon to rise? In what respect is hydrogen better than helium for balloons? In what respects is helium better?
15. A balloon contains 800,000 litres of hydrogen. What is the weight of this volume of hydrogen? What is the weight of an equal volume of air? (One litre of air weighs 1.293 grams.)
16. How many grams of hydrogen could be obtained by the action of an excess of dilute sulphuric acid on 10 grams of mossy zinc?

Chapter XIII

THE GAS LAWS

1. Measurement of Gases

Much of the work in elementary chemistry has to do with gases and so it would be well at this point to consider carefully the nature of gases and some of the important laws governing their behaviour.

All gases have weight but it is difficult to determine this property exactly. It is much easier to determine the volume of a gas and that is the usual method of measuring gases. This is done by collecting the gas by the downward displacement of water in a graduated gas measuring tube or in a tall graduated cylinder. The volume of water displaced gives us a measure of the volume of the gas. The volume of a gas is changed greatly by two factors:

(1) *Pressure.*
(2) *Temperature.*

It has been found that there are certain rules or laws concerning the effect of *pressure* and *temperature* upon the volume of a gas. These laws will be considered carefully in this chapter as it is important to know the behaviour of gases under different conditions, when one studies them in the laboratory. It should be recalled that a law, in science, is a statement of a fact which can be shown to be true by experiment or observation.

2. Boyle's Law

This law, which was discovered by the great Irish scientist Robert Boyle in 1660, has to do with the effect of *pressure* upon the *volume* of a gas.

In measuring the pressure of a gas some *standard* is necessary and many years ago scientists selected the average pressure of the air at sea level for this purpose. At sea level, the average pressure of the atmosphere is 14.7 pounds per square inch or 1033.6 grams per square centimetre. This means that the weight of air over one square inch of the earth's surface at sea level is 14.7 pounds. This pressure can support a column of mercury about 30 inches (or 76 centimetres or 760 millimetres) in height. In scientific work pressure is measured in centimetres or millimetres of mercury and 76 cm. or 760 mm., which is the pressure exerted by the air at sea level, is known as *standard pressure.* It is also called *one atmosphere of pressure.*

The pressure of the atmosphere is measured by an instrument called the *barometer.* The first measurement of the pressure of the air was made in 1643 by Torricelli who used an apparatus similar to the one shown in Fig. 55. A tube about three feet long and closed at one end was filled with mercury. Then the open end was closed with the thumb to prevent the escape of mercury and the tube was inverted and placed with its open end below the surface of mercury in a dish, after which the thumb was withdrawn. The mercury dropped at once in the tube until it stood at a height of about 30 inches or 760 millimetres above the level of the mercury in the dish. The space above the mercury in the tube was a vacuum except for the presence of a very small amount of mercury vapour. This instrument is known as a *simple barometer* and all other types of barometers are calibrated by means of a mercury barometer. It is the pressure of the air on the mercury in the dish which holds up the column of mercury in the tube; hence, the rise and fall of the mercury within the tube is proportional to the increase and decrease of the pressure of the atmosphere.

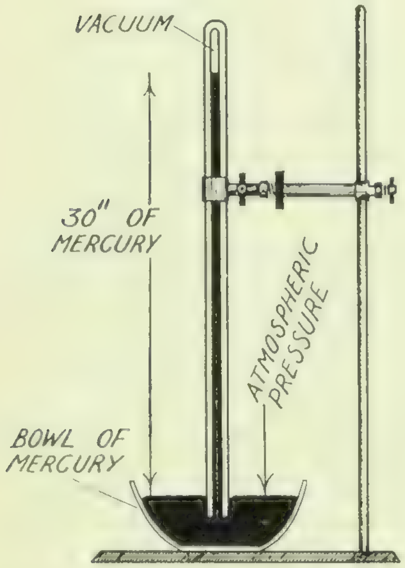


FIG. 55—SIMPLE BAROMETER

Boyle did many experiments concerning the effect of pressure upon the volume of a gas but we shall not attempt to describe the apparatus which he used or any of the details of his experiments. The following illustration of what happens to the volume of a gas when various pressures are applied, is typical of the experimental results which Boyle obtained in his work. Suppose we start with 12 litres of a gas under a pressure of *one* atmosphere as shown in Fig. 56. When *two* atmospheres of pressure are applied the volume decreases to *one-half* its original volume and when *three* atmospheres are applied the volume decreases to *one-third* its original volume. The application of *four* atmospheres changes the volume to *one-fourth* of what it was at the beginning. Now, in mathematics, it is found that the inverse of 2 is ½, of 3 is ⅓ and of 4 is ¼. From a study of this example, it is apparent that *the volume of a given mass of a gas varies inversely as the pressure, the temperature remaining constant.* This is a statement of *Boyle's Law* and it is used a great deal by chemists when studying gases.

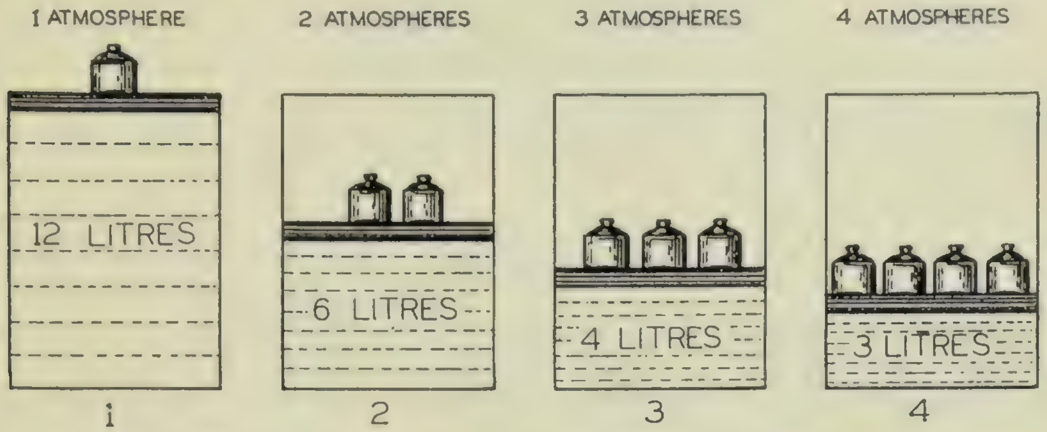


FIG. 56—DIAGRAMMATIC ILLUSTRATION OF BOYLE'S LAW

This law can be expressed mathematically as follows:

$$V_1P_1 = V_2P_2 = V_3P_3 = V_4P_4 = K \text{ (constant)}$$
$$12 \times 1 = 6 \times 2 = 4 \times 3 = 3 \times 4 = 12$$

In most problems in chemistry there are only two pressures and two volumes involved and so the following formula is generally used.

$$V_1P_1 = V_2P_2$$

where V_1 = volume at start
P_1 = pressure at start
V_2 = volume at end
P_2 = pressure at end

The following examples will illustrate the use of this law.

EXAMPLE I

A gas measures 100 c.c. under a pressure of 760 mm. What will its volume be under a pressure of 380 mm.?

$$V_1P_1 = V_2P_2$$
$$100 \times 760 = V_2 \times 380$$
$$76000 = 380\ V_2$$
$$\text{or } V_2 = \frac{76000}{380} = 200 \text{ c.c.}$$

Example II

A gas measures 500 c.c. at one atmosphere of pressure. What will be its volume at 2000 mm. of pressure

$$\begin{aligned} V_1P_1 &= V_2P_2 \\ 500 \times 760 &= V_2 \times 2000 \\ 380{,}000 &= 2000\ V_2 \\ \text{or } V_1 = \frac{380{,}000}{2000} &= 190 \text{ c.c.} \end{aligned}$$

EXERCISES

1. A gas measures 200 c.c. under a pressure of 760 mm.
   What is its volume: (1) at 190 mm.?
   (2) at 95 mm.?
   (3) 1 mm.?
   (4) 700 mm.?
   (5) 1000 mm.?
2. A gas measures 1200 c.c. at 1 atmosphere of pressure. What is its volume at 100 atmospheres?
3. A gas has a volume of 600 c.c. at 740 mm. What is its volume at 1 atmosphere?
4. How many pounds pressure would be required to force 100 cubic feet of coal gas at 20 lbs. pressure into 1 cubic foot?
5. A gas has a volume of 1 litre at standard pressure. What will be its volume at 800 mm. pressure?

3. Charles' Law

This law has to do with the effect of temperature upon the volume of a gas. It is a well-known fact that most substances expand when heated and contract when cooled. Everyone is familiar with the expansion and contraction of mercury in a thermometer with changes of temperature. Gases, when warmed or cooled, vary in volume much more than liquids. For example, air when heated expands about nine times more than water.

It was more than a hundred years after the time of Boyle that this change in the volume of a gas, when heated or cooled. was studied carefully by the French chemist Charles. In 1787 he found that, if the pressure remained the same, the volume of any gas at 0° C. increases 1/273 of its volume for every degree rise in centigrade temperature and the volume decreases to the same extent for every degree drop in centigrade temperature.

Suppose, for convenience, we start with 273 c.c. of a gas at 0° C. as shown in the table below.

Table 5—The Effect of Temperature on Volume of a Gas

Temperature Change	Increase of Volume	New Volume
0° to 1° C.	$\frac{1}{273} \times 273$ c.c. = 1 c.c.	273 + 1 = 274 c.c.
0° to 10° C.	$\frac{10}{273} \times 273$ c.c. = 10 c.c.	273 + 10 = 283 c.c.
0° to 100° C.	$\frac{100}{273} \times 273$ c.c. = 100 c.c.	273 + 100 = 373 c.c.
0° to 273° C.	$\frac{273}{273} \times 273$ c.c. = 273 c.c.	273 + 273 = 546 c.c.
	Decrease of Volume	
0° to −1° C.	$\frac{1}{273} \times 273$ c.c. = 1 c.c.	273 − 1 = 272 c.c.
0° to −10° C.	$\frac{10}{273} \times 273$ c.c. = 10 c.c.	273 − 10 = 263 c.c.
0° to −100° C.	$\frac{100}{273} \times 273$ c.c. = 100 c.c.	273 − 100 = 173 c.c.
0° to −273° C.	$\frac{273}{273} \times 273$ c.c. = 273 c.c.	273 − 273 = 0 c.c.

An examination of the above table shows that an increase of temperature from 0° to 273° C. doubles the original volume but a decrease of temperature from 0° to −273° C. decreases the volume to zero. Of course, it is impossible for a gas to disappear completely and this is never realized in the laboratory. No material can exist in the form of a gas at −273° C. as all substances change to a liquid at that temperature. The theoretical disappearance of a gas at this temperature means that it is not the volume of the gas itself that is reduced to zero, but the space between the molecules.

Some years ago scientists devised a temperature scale, using −273° C. as the zero point. This system of expressing temperatures is called the *absolute temperature scale* and −273° C. is called *absolute zero.* A study of Fig. 57 shows that a centigrade reading can be changed to the corresponding absolute reading by the addition of 273. Thus, 20° C. is equal to

293° A. (273 + 20) and −20° C. is equal to 253° A. (273 − 20). Chemists find this absolute temperature scale, which is sometimes called the Kelvin scale, very useful in calculating changes in volumes of gases due to changes in temperature.

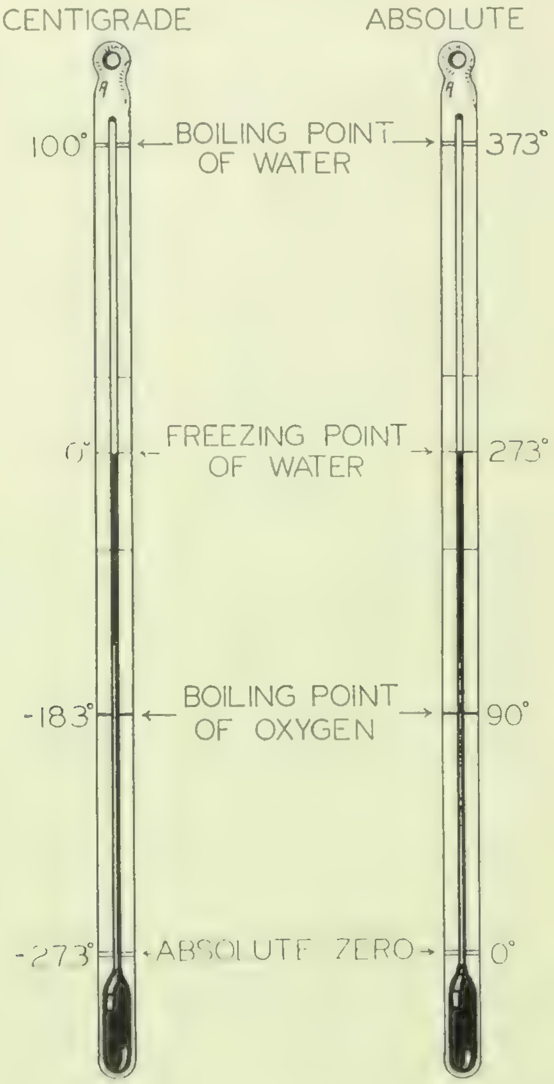


Fig. 57—A comparison of Centigrade and Absolute Temperature Scales

If we examine the information given in the table on page 87 again and arrange these facts in another table as shown on page 89, the relationship between the volume of a gas at constant pressure and the absolute temperature is demonstrated. A study of the above table shows that *the volume of a given quantity of a gas varies directly as the absolute temperature, the pressure remaining constant.*

Chemists usually call this Charles' law but some physics

TABLE 6—THE RELATIONSHIP BETWEEN THE VOLUME OF A GAS AND THE ABSOLUTE TEMPERATURE

Temperature (Degrees Centigrade)	Temperature (Degrees Absolute)	Volume (Cubic Centimetres)
0	273 + 0 = 273	273
1	273 + 1 = 274	274
10	273 + 10 = 283	283
100	273 + 100 = 373	373
273	273 + 273 = 546	546
−1	273 − 1 = 272	272
−10	273 − 10 = 263	263
−100	273 − 100 = 173	173
−273	273 − 273 = 0	0

books refer to it as *Gay-Lussac's law.* This law can be expressed mathematically as follows:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\text{or } V_1T_2 = V_2T_1$$

where V_1 = volume at start.
T_1 = *absolute* temperature at start.
V_2 = volume at end
T_2 = *absolute* temperature at end.

The following examples will illustrate the use of this law.

EXAMPLE I

A gas has a volume of 600 c.c. at 27° C. What will its volume be at 127° C.?

$$T_1 = 27 + 273 = 300^\circ \text{ Absolute.}$$
$$T_2 = 127 + 273 = 400^\circ \text{ Absolute.}$$
$$V_1 = 600 \text{ c.c. and } V_2 = \text{the unknown.}$$
$$V_1T_2 = V_2T_1$$
$$600 \times 400 = V_2 \times 300$$
$$V_2 = 600 \times \frac{400}{300} = 800 \text{ c.c.}$$

EXAMPLE II

A gas has a volume of 300 c.c. at 27° C. What will its volume be at −73° C.?

$$T_1 = 27 + 273 = 300^\circ \text{ Absolute.}$$
$$T_2 = -73 + 273 = 200^\circ \text{ Absolute.}$$

$$\begin{aligned} V_1 &= 300 \text{ c.c.} \\ V_2 &= \text{the unknown.} \\ V_1T_2 &= V_2T_1 \\ 300 \times 200 &= V_2 \times 300 \\ V_2 &= \frac{300 \times 200}{300} = 200 \text{ c.c.} \end{aligned}$$

EXERCISES

1. A gas has a volume of 546 c.c. at 0° C. What will be its volume at 27° C.?
2. A gas occupies a volume of 1200 c.c. at 127° C. What will be its volume at −173° C.?
3. A gas has a volume of 200 c.c. at 27° C. To what temperature on the centigrade scale must this gas be heated to double its volume?
4. A gas has a volume of 600 c.c. at a temperature of 27° C. To what temperature centigrade must it be heated to change the volume of of this gas to 900 c.c.?
5. A gas has a volume of 1000 c.c. at 273° C. What will be its volume at 0° C.?

4. Standard Conditions

Many years ago chemists decided that 0° C. or 273° A. and 760 mm. pressure should be the standard conditions for any gas. These conditions are usually designated by the following abbreviation:

S.T.P. (standard temperature and pressure.)

5. The Gas Equation

In practice the chemist usually has to make corrections for *both* the pressure and the temperature in reducing the volume of a gas to standard conditions. The laws of Boyle and Charles have been combined into one equation called the *gas equation*. It is as follows:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

It will be observed that when $T_1 = T_2$ (temperature is constant) that the gas equation becomes

$$P_1V_1 = P_2V_2 \text{ (Boyle's Law).}$$

It will also be observed that when

$$P_1 = P_2 \text{ (pressure is constant)}$$

that the gas equation becomes

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ (Charles' Law).}$$

The following examples will illustrate the use of the *gas equation.*

EXAMPLE I.

A gas occupies 250 c.c. when measured at a pressure of 700 mm. and at $-23°$ C. What will be its volume at 350 mm. and at 27° C.?

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{700 \times 250}{250} = \frac{350 \times V_2}{300}$$

$$V_2 = \frac{700 \times 250 \times 300}{250 \times 350} = 600 \text{ c.c.}$$

This problem can also be solved without the use of the gas equation. It can be reasoned through as follows: the pressure is to change from 700 mm. to 350 mm., that is, it is to become less; then the volume of the gas will become greater; so it is necessary to multiply by a fraction that will make it greater. In this case the fraction is $\frac{700}{350}$. Similarly, with the temperature: from $-23°$ C. ($-23 + 273 = 250°$ A.) to 27° C. ($27 + 273 = 300°$ A.) is an increase of temperature, accompanied by an expansion of the gas; so our fraction must be greater than one. It is $\frac{300}{250}$. The new volume of the gas can be found by calculating the following expression:

$$250 \times \frac{700}{350} \times \frac{300}{250} = 600 \text{ c.c.}$$

It is often helpful to beginners if they tabulate the facts given in a gas law problem as follows:

$V_1 = 250$ c.c.	$V_2 = X$ c.c.
$P_1 = 700$ mm.	$P_2 = 350$ mm.
$T_1 = 250°$ A.	$T_2 = 300°$ A.

From this, using the same reasoning as given above, we get the equation:

$$X = 250 \times \frac{700}{350} \times \frac{300}{250} = 600 \text{ c.c.}$$

EXAMPLE 2.

A gas occupies 1200 c.c. at 27° C. and a pressure of 380 mm. of pressure. What will its volume be at S.T.P.?

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{380 \times 1200}{300} = \frac{760 \times V_2}{273}$$

$$V_2 = \frac{380}{760} \times \frac{273}{300} \times 1200 = 546 \text{ c.c.}$$

Instead of using the gas law equation, the above problem can be solved by tabulation of the information given and then thinking it through as described above. The tabulation is as follows:

V_1 = 1200 c.c.	V_2 = X cc.
P_1 = 380 mm.	P_2 = 760 mm.
T_1 = 300° A.	T_2 = 273° A.

$$X \text{ c.c.} = 1200 \times \frac{380}{760} \times \frac{273}{300} = 546 \text{ c.c.}$$

6. Diffusion of Gases

Everyone knows that a toy balloon filled with air or hydrogen slowly becomes deflated because the gas molecules pass through the material of which the balloon is made. When a bottle of hydrogen is placed mouth downward over a bottle of air, a mixing of the two gases takes place. The very light molecules of hydrogen move downward, and in time the two gases become evenly mixed. The above examples show that molecules of gases move about in all directions and this phenomenon is known as *diffusion.* The lighter the gas is, the faster will its molecules move. Since hydrogen is the lightest gas known, its diffusion is faster than that of all other gases. This property of diffusion is one of the important experimental facts which support the idea that gases are composed of very small particles, called molecules, which are in rapid motion.

7. How the Molecular Theory Explains the Gas Laws

(a) BOYLE'S LAW. According to the molecular theory a gas is made up of a large number of *molecules* which possess *kinetic energy*. If a gas is enclosed in a vessel, the molecules of the gas bombard the walls of the vessel continuously and the sum of all these impacts of the molecules against the walls produces an effect which is known as the pressure of the gas. Now let us consider a gas which is confined in a vessel with a movable piston as shown in Fig. 58. The weight on the piston just balances the pressure produced by the bombardment of the gas molecules from beneath. Suppose the piston is forced down until the volume is one-half of what it was at the beginning. Exactly the same number of molecules are still present and they move with the same speed. However, they travel only half as far before hitting the walls of the vessel, and so they bombard any given area twice as often as before. In other words, the number of molecules per unit volume has been doubled in this case, and so there would be twice as many impacts on a square centimetre of wall surface per second. Thus, the pressure of the gas is double its original pressure and in order to prevent the gas from expanding it is necessary to double the weight on the piston. The volume of the gas

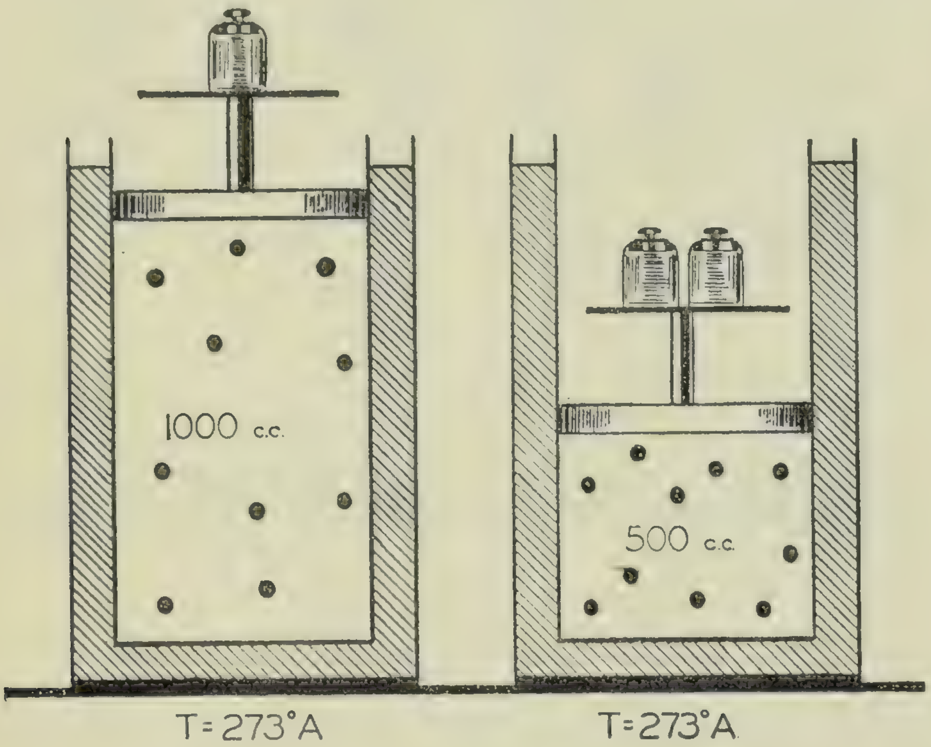


FIG. 58—EXPLANATION OF BOYLE'S LAW

varies inversely as the pressure, and hence the idea of molecules can explain Boyle's law.

(b) CHARLES' LAW. Now let us consider the effect of heat upon the volume of a gas. Heat is a form of energy and hence when it is added to a gas the molecules will move faster. If a gas is enclosed in an apparatus as shown in Fig. 59, then when heat is applied the molecules will strike a unit area of the underside of the piston a greater number of times per second. In other words, the pressure of the gas will increase. If the weight upon the piston remains the same, then the pressure of the gas will push it upwards until the increased volume makes the path of the molecules just long enough to overcome the effect of their increase in speed. Thus the molecular theory explains the law of Charles.

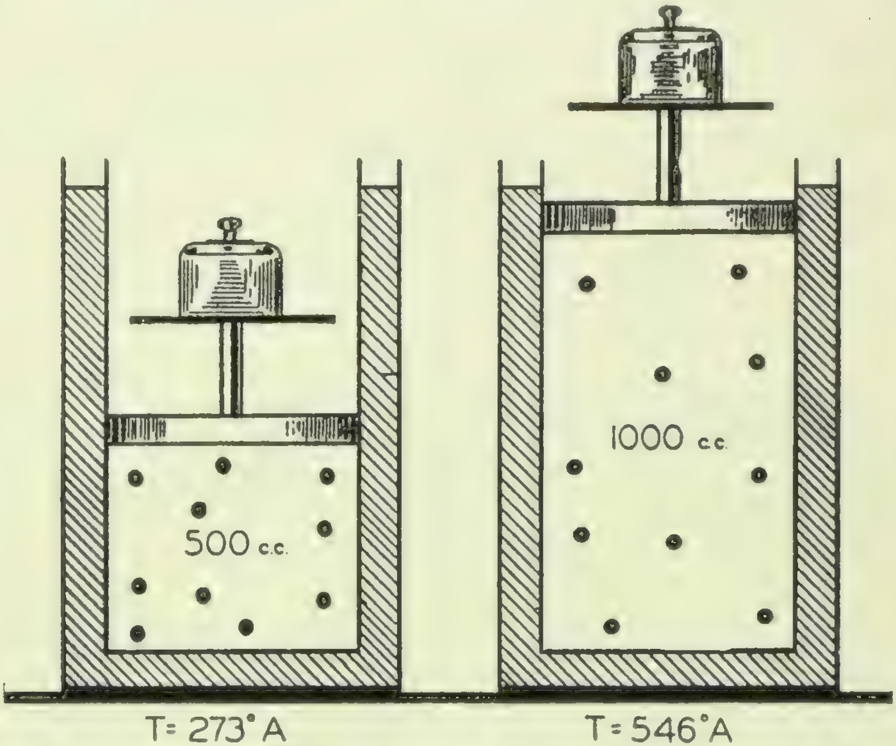


FIG. 59—EXPLANATION OF CHARLES' LAW

EXERCISES

1. A gas occupies 150 c.c. when measured at a pressure of 700 mm. and at a temperature of −23° C. What will be its volume at a pressure of 800 mm. and a temperature of 27° C.?
2. A gas has a volume of 800 c.c. at 720 mm. and 25° C. What will be its volume at 780 mm. and 20° C.?
3. A gas has a volume of 1 litre under 740 mm. and 17° C. What will be its volume under 780 mm. and at 27° C.?

4. A quantity of hydrogen measures 320 c.c. under 750 mm. and at 20° C. What will be its volume at S.T.P.?
5. Reduce the following gas volumes to S.T.P.:
   (a) 150 c.c. at 380 mm. and 18° C.
   (b) 270 c.c. at 1520 mm. and 300° C.
6. A certain quantity of oxygen measures 1 litre at S.T.P. What will be its volume at 20° C. and 725 mm.?
7. If 2000 c.c. of a gas is collected at −20° C. and a pressure of 720 mm., what volume will it occupy at 233° C. and a pressure of 1440 mm.?
8. An automobile tire was inflated at 30 lbs. pressure when the temperature was 20° C. Assuming no change in volume, what will the pressure become when the temperature rises to 40° C.?
9. If 200 litres of air are measured at 20° C. and 740 mm., find the volume of the air at S.T.P.
10. A quantity of gas is found to measure 840 c.c. when the barometer is at 750 mm. and the temperature is 15° C. The next day the barometer is 765 mm. and the temperature is 10° C. What is the volume then?

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CHAPTER XIV

WATER

1. Occurrence and Importance

Water is the most familiar of all chemical compounds. Chemists have shown that it is formed by the union of the gas hydrogen with the gas oxygen in the proportion of two volumes of hydrogen to one volume of oxygen, its chemical formula being H_2O. Water originates in nature from the water vapour of the earth's atmosphere, the various physical forms of which are familiar to all as clouds, mists, dew, rain, snow, hail and ice. Plants and animals contain a high proportion of water and it is essential to all life. The human body contains about 70% water. Water also makes up a large part of most foods. For instance, flour has a water content of 12%, beef 62%, apples 80%, milk 87%, watermelons 92% and cucumbers 95%. All soils contain water which is so vital to the growth of plants. Agricultural scientists tell us that from 30 to 120 gallons of water are needed to produce one pound of dry plant material.

2. Physical Properties

(1) Water is a *liquid* above 0° C. and below 100° C. at ordinary pressures.

(2) It is a colourless *liquid* in thin layers but appears greenish-bluish when observed through considerable thickness.

(3) Pure water is *odourless* and *tasteless*.

(4) *One cubic centimetre of water at 4° C. weighs one gram*, which is the unit of density.

(5) Water is the *most widely used of all solvents*. It dissolves a greater number of substances than any other liquid.

(6) The *freezing point* (f.p.) of pure water is 0° C. and the *boiling point* (b.p.) of water is 100° C. at a pressure of 760 mm.

(7) *The heat capacity* of water, which means its power to hold heat, is higher than that of any other substance. The amount of heat required to raise the temperature of 1 gram of water through 1° C. is called the *calorie*, and is the unit used in the measurement of *quantities of heat*. The heat capacity of water makes it very useful for certain purposes. For example, in hot-water heating systems, water is the best as well as the

cheapest liquid which could be used. The effect of large bodies of water upon the climate of regions near them is very marked, and this is due to the high heat capacity of water. In winter a large body of water cools slowly and gives off large quantities of heat in the process. This heat stops the land temperature from falling as low as it otherwise would. In summer, the large expanse of water absorbs much heat tending to prevent extremes of temperature on nearby land.

(8) Expansion and Contraction of Water. The general rule regarding the expansion and contraction of substances is, that materials expand on heating and contract on cooling. Water, however, does not obey this rule between 0° C. and 4° C. When water is cooled from 4° C. to 0° C., it expands instead of contracting. The data shown in the following table helps to make clear this abnormal behaviour of water between 0° and 4° C.

Table 7—Relative Density and Volume of Water

Temperature °C.	Density	Volume
80	0.97183	1.02899
60	0.98324	1.01705
40	0.99224	1.00782
20	0.99823	1.00177
10	0.99973	1.00027
8	0.99988	1.00012
6	0.99997	1.00003
4	1.00000	1.00000
2	0.99997	1.00003
0	0.99987	1.00013

The relations between the volume and temperature of water is shown graphically in Fig 60. A study of this graph shows that water, at temperatures above 4° C., behaves like most liquids, expanding when heated and contracting when cooled. Below 4° C., however, the curve is abnormal.

Examination of Table 7 shows that the expansion of water when cooled from 4° C. to 0° C. is, indeed, very small. However, this fact has a very marked effect upon climate and so upon all forms of life. For example, when the water on the surface of a lake becomes cold, it contracts. Cold water is heavier than warm water and so the warm water rises and the cold water sinks. This circulation of the water gradually cools down the temperature of the lake to 4° C. Table 7 shows that water, cooled below 4° C., has a density of less than one. Thus, cooling of the lake below 4° C. results in the cooler water rising to the surface instead of sinking as it did above 4° C.

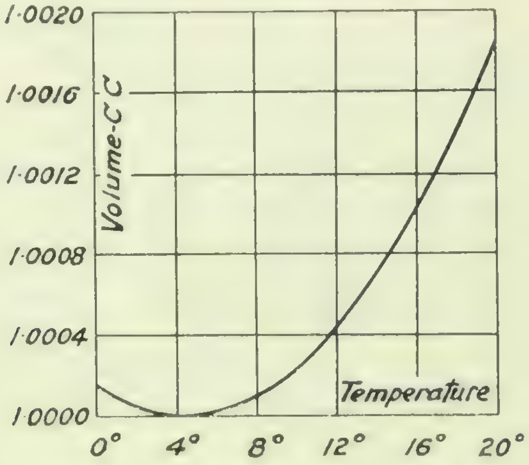


Fig. 60—A Graph to Show the Relations Between the Volume and Temperature of Water

Finally, when the temperature of the air drops to 0° C., a film of ice is formed on the surface of the lake. If we did not have expansion of the water in this manner, as the temperature dropped to 0° C., the entire body of water would freeze from the bottom upwards and bring about marked changes in climate, because the greater quantities of ice produced in winter would greatly influence the temperature of the atmosphere during the other seasons of the year.

At 0° C. water changes to the solid state (ice) and in doing so expands considerably. For example, 100 c.c. of water at 0° C. produces about 110 c.c. of ice at the same temperature. The density of ice at 0° C. is about 0.92, whereas the density of water at 0° C. is very slightly less than one and so ice floats in water. The expansion of water during freezing plays an important part in the weathering and decay of rocks in countries exposed to alternate frost and thaw. Water freezing in the surface crevices of rocks splits and widens the openings so that the surface crust of the rock appears to break up during a "thaw."

Although water expands on changing from the liquid to the solid state, ice behaves like a normal substance, contracting on cooling and expanding on heating. It has been reported that at −60° C. the density of ice is greater than that of water, and ice at that low temperature sinks in water.

3. Chemical Properties

(1) The Stability of Water. Water is a relatively stable compound. Compounds which are not easily decomposed by heat even at very high temperatures are said to be stable. Thus, water at 2000° C. and a pressure of 1 atmosphere will only decompose to the extent of about 10 per cent.

(2) Water Reacts with Metals. Water reacts with active metals, such as sodium and calcium, to produce hydrogen gas and a base.

$$2\,Na + 2\,HOH \longrightarrow 2\,NaOH + H_2\uparrow$$

$$Ca + HOH \longrightarrow Ca\,(OH)_2 + H_2\uparrow$$

(3) Water does not burn and it does not support combustion.

(4) Water reacts with Certain Oxides. The reaction of water with the oxides of the metallic elements to form bases was considered in the chapter on oxygen. For example, calcium oxide (quick lime) combines with water to form calcium hydroxide (slaked lime).

$$CaO + HOH \longrightarrow \underset{\text{(Calcium hydroxide)}}{Ca(OH)_2}$$

Water reacts with the oxides of non-metallic elements to form acids. Carbon dioxide, for example, reacts with water to form carbonic acid.

$$CO_2 + H_2O \longrightarrow \underset{\text{(carbonic acid)}}{H_2CO_3}$$

4. Tests for Pure Water

(a) Physical. Pure water should have a boiling point of 100° C. at 760 mm. of pressure and it should freeze at 0° C.

(b) Chemical. The usual chemical test for water is to add a few drops to some powdered *anhydrous copper sulphate*, which turns from white to blue in colour.

$$\underset{\substack{\text{anhydrous copper}\\ \text{sulphate (white)}}}{CuSO_4} + 5\,H_2O \longrightarrow \underset{\substack{\text{hydrated copper}\\ \text{sulphate (blue)}}}{CuSO_4.\,5\,H_2O}$$

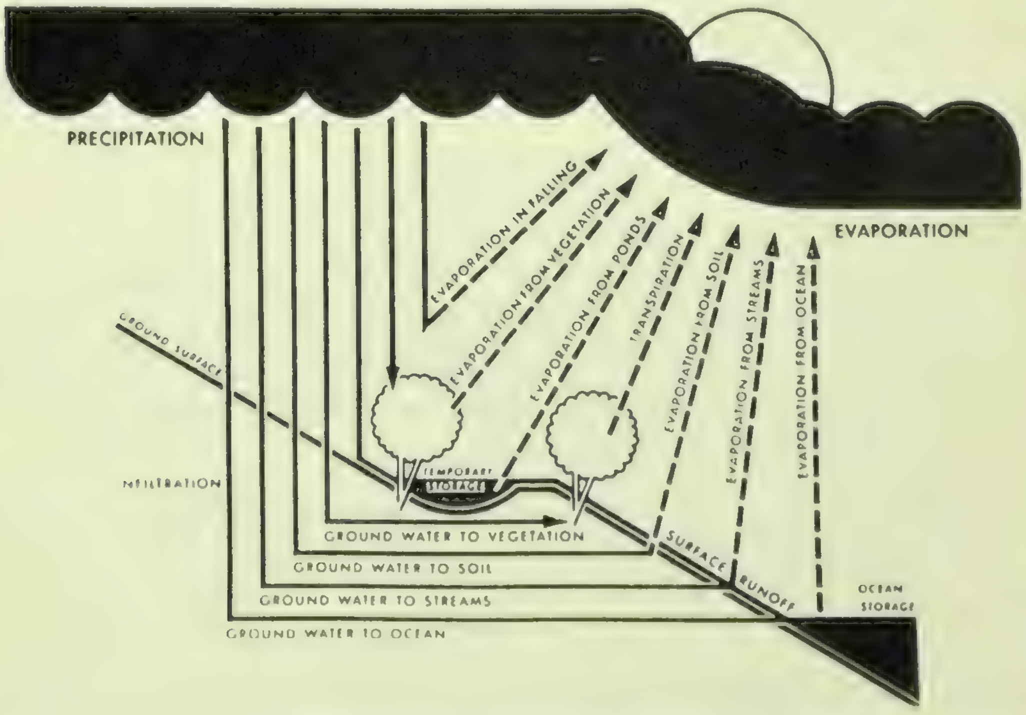
5. The Water Cycle

All life depends on the continuous circulation of water. In the first place, water leaves the surface of the earth in the form of vapour and then, in time, it returns to the earth's surface again in precipitation. Water is continually evaporating from the surface of the sea and it dissolves in or diffuses through the air. The winds carry the water vapour into the upper air and here it is condensed to form clouds, returning to the land as rain.

If rain falls directly into the sea, the cycle is completed at once. When water falls upon the land, the return of the water to the sea from whence it came may occur in a short period of time or it may take years. It may stand on the surface, as in a swamp or lake; or it may go underground, to return to the surface as a spring. Much of the water which falls to the earth as rain evaporates again into the air. At any rate, in time it will find its way back to the ocean.

In streams and rivers, which carry along many kinds of minerals both in solution and as suspended materials, such as solid particles of rock, clay or organic substances, the water at last reaches the sea. Thus, the waters of the ocean, although constantly evaporating, do not become smaller in volume.

This cycle is not necessarily completed in one stage. Indeed, it is usually a series of changes, from water to vapour, from vapour to rain, from surface water to vapour again, not once but many times. Scientists call this phenomenon the *hydrologic cycle.* The idea is pictured graphically in Fig. 61.



Courtesy of Soil Conservation Service, U.S. Dept. of Agriculture

FIG. 61—THE HYDROLOGIC CYCLE

6. Impurities in Natural Waters

From a study of the water cycle it is evident that there are a number of impurities in natural waters. These substances found in natural waters are of two types, *dissolved* and *suspended* materials.

(1) DISSOLVED IMPURITIES. Since water is such an excellent solvent, it is never found pure in nature. Sea water, for example, has a considerable amount of common salt and many other substances dissolved in it. Water from rivers, wells or springs, often contains mineral matter in solution. These materials were dissolved by the water as it flowed through the soil or over rocks. Such water does not have the flat taste of rain-water or of water which has been distilled. Certain of these dissolved mineral substances combine with soap to form a sticky insoluble material, which is usually called *curd.* Water containing such mineral materials is known as *hard water* because of the difficulty of forming a lather with it when a soap solution is added. Distilled and rain-water, which are almost free of dissolved minerals, form a lather readily and they are called *soft water.* In any household where hard water is used, a scum may be observed when soap is used in the water.

In large laundries, in artificial ice plants or in factories where large quantities of water are boiled to produce steam, the use of hard water would cause a great deal of trouble and expense. In many such plants the water is softened by the addition of inexpensive chemicals. These chemical compounds react with the harmful dissolved minerals in the natural water to produce insoluble substances, which are removed by filtration.

Water from certain wells and springs contains only a small amount of dissolved material; but the purest form of natural water is rain water. Even this water, however, contains gases dissolved from the air, such as oxygen and carbon dioxide.

(2) SUSPENDED IMPURITIES. In addition to the dissolved impurities, natural water usually has a great deal of material suspended in it. This generally consists of very fine particles of soil and causes what is commonly called "muddy water." Still another kind of impurity is organic matter, which is partially suspended and partially dissolved, and consists of compounds produced by plants and animals. These come from the plant life in the soil and from sewage. Along with the organic material and living matter on it, are micro-organisms or bacteria, many of which cause disease. The presence of these

harmful bacteria in water is usually due to contamination with the waste products of animal life. Certain diseases, such as typhoid fever, are often contracted by drinking water which is polluted in such a manner and into which the typhoid bacteria have found their way. Because water contaminated with sewage is very dangerous, towns and cities must take great care to obtain their water supply from uncontaminated sources, and if this is impossible, the water which is used must be carefully purified. In addition to the above mentioned suspended impurities, there is always a certain amount of dust from the air in natural waters.

(3) Water Analysis. From a study of the impurities present in natural waters it is evident that great care must be taken in the selection of water for washing and drinking purposes. If water is secured from a well, a sample of the water should be sent to the proper health authorities for examination. There the water is usually examined for the presence of harmful bacteria as well as for its mineral content. Some well waters contain so much dissolved mineral material that they are unsuitable for use by humans or animals. Of course, if the water contains harmful bacteria, it should never be used even for washing purposes.

7. The Purification of Water

The purification of water is very important. There are a number of methods which can be used to purify water and these will now be considered briefly.

(1) Settling and Decantation. Perhaps the simplest method of purifying water is settling and decantation. It consists of allowing water to stand for some time so that the suspended impurities such as fine sand, clay or organic matter, may settle to the bottom of the container. The clear water can be poured off from the sediment at the bottom or, if the container is very large, the water can be siphoned off. This method does not remove the bacteria or dissolved minerals.

(2) Boiling. Water which contains harmful bacteria may be made fit to drink by boiling for a short time. This method does not remove any of the impurities but merely kills the micro-organisms which cause disease. These very small forms of life cannot live at the temperature of boiling water.

(3) Distillation. All the dissolved and suspended materials can be removed by a process called distillation. The

impure water is boiled in a vessel, which is so arranged that the steam will pass through a cold tube, where it returns to the liquid state. This change of water from vapour to liquid is called *condensation* and the apparatus in which it takes place is called a *condenser*. The water which drops from the end of the condenser is pure, the mineral impurities being left behind in the vessel in which the water was boiled. Water purified in this way is called *distilled water* and it is used in the laboratory when pure water is desired. This method would not remove soluble volatile impurities because they would be driven over with the steam and mixed with water in the *distillate*, which is the name given to the liquid which drops from the lower end of the condenser. For example, water containing ammonia gas in solution cannot be purified by distillation. As a rule, however, most natural waters can be purified by distillation, which is the best method of purifying water. However, it is not practical to purify large supplies of water for towns or cities by this means.

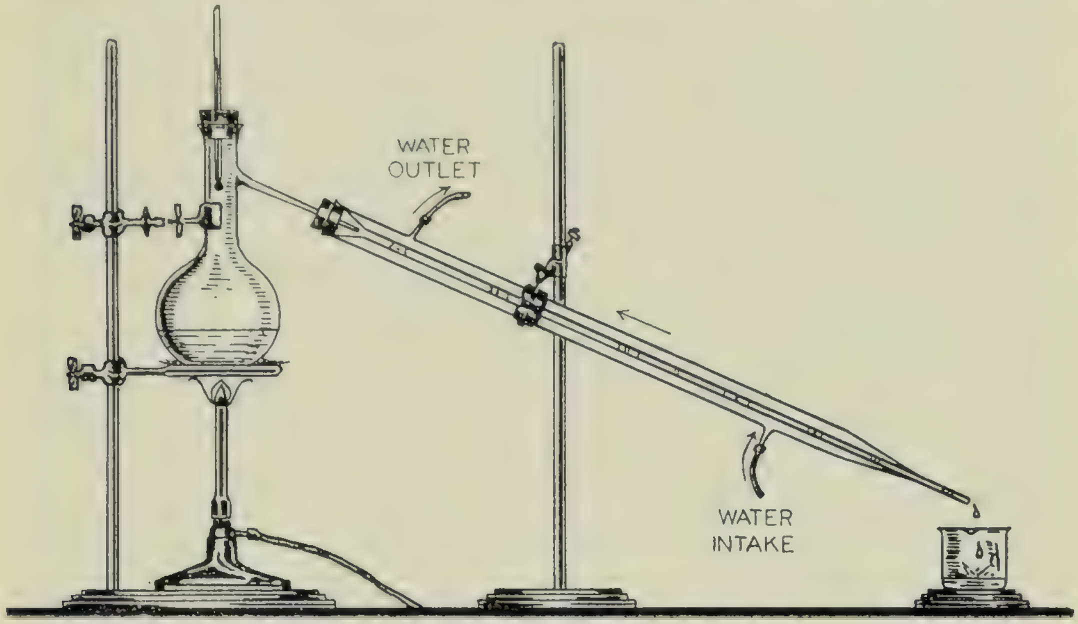


Fig. 62—A Liebig Condenser Used for Distillation

(4) Filtration. The suspended material in water may be removed by filtration. This is done on a large scale in cities where the only supply comes from muddy rivers or similar sources. The water is allowed to pass slowly through beds of gravel and sand as shown in Fig. 63. The suspended material is caught between the small particles of the sand and retained. The water coming through at the bottom of the filter bed still contains all the *dissolved* impurities. but it is free from suspended

matter and is much more suitable for household uses. Settling basins are generally used in connection with the filter beds to remove most of the mud, clay or sand, which otherwise would collect in the filter beds and slow up the passage of water. The filtration process does not remove all the harmful bacteria and so some chemical method, such as chlorination, is usually combined with this method of purification.

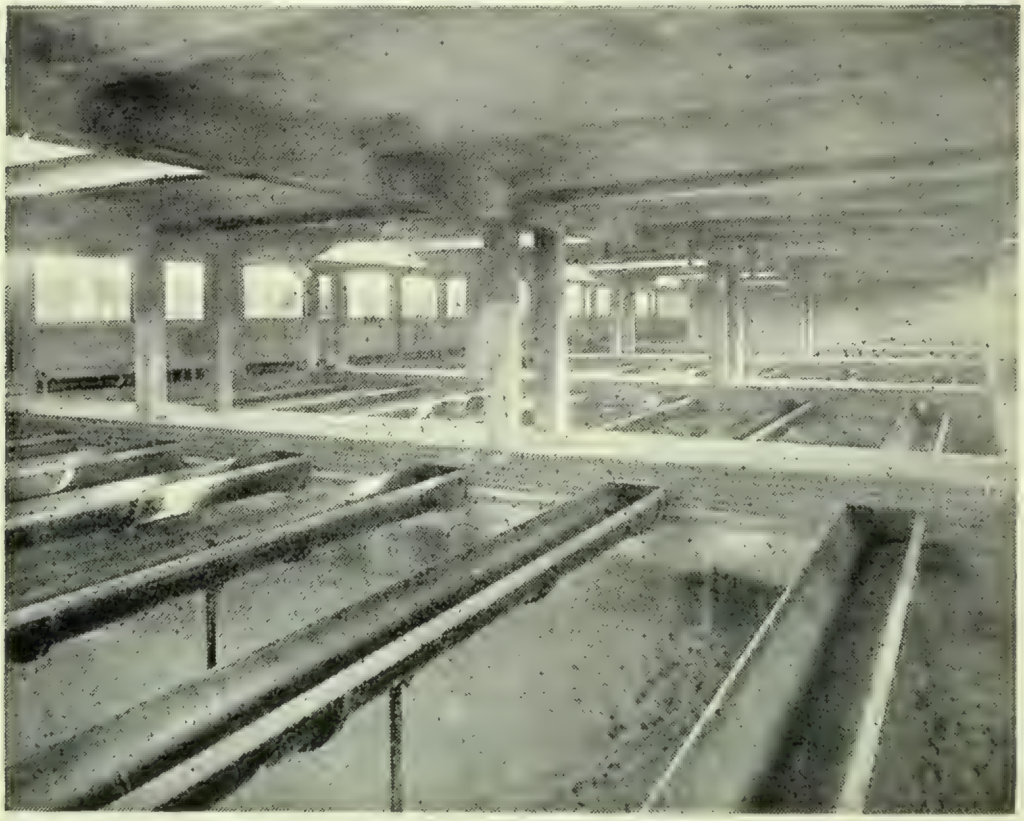


Fig. 63—Rapid Sand Filters, Ottawa

The open troughs carry off the water used in back-washing.

(5) Chemical Treatment. A number of chemical substances, when added to water in very small amounts, destroy the bacteria. Chlorine is used in many cities and towns for this purpose. It has been found that a concentration of chlorine not larger than 0.3 to 2 grams of the gas per million grams of water is sufficient to kill all germs. The effect of chlorination has been very marked in the reduction of the death rate from typhoid fever.

When water is exposed to the air, the oxygen oxidizes much of the organic matter and destroys some of the bacteria. Natural waters dissolve oxygen and in time purify themselves. This is a slow process, but in a slightly different form, has been used to some extent for purifying city water. The water is sprayed into the air in fountains, thus allowing as much opportunity as possible for the chemical action of the oxygen of the air. This process is sometimes called *aeration.*

Alum is often added to natural water in the settling basins as it hastens the settling down of much of the suspended material.

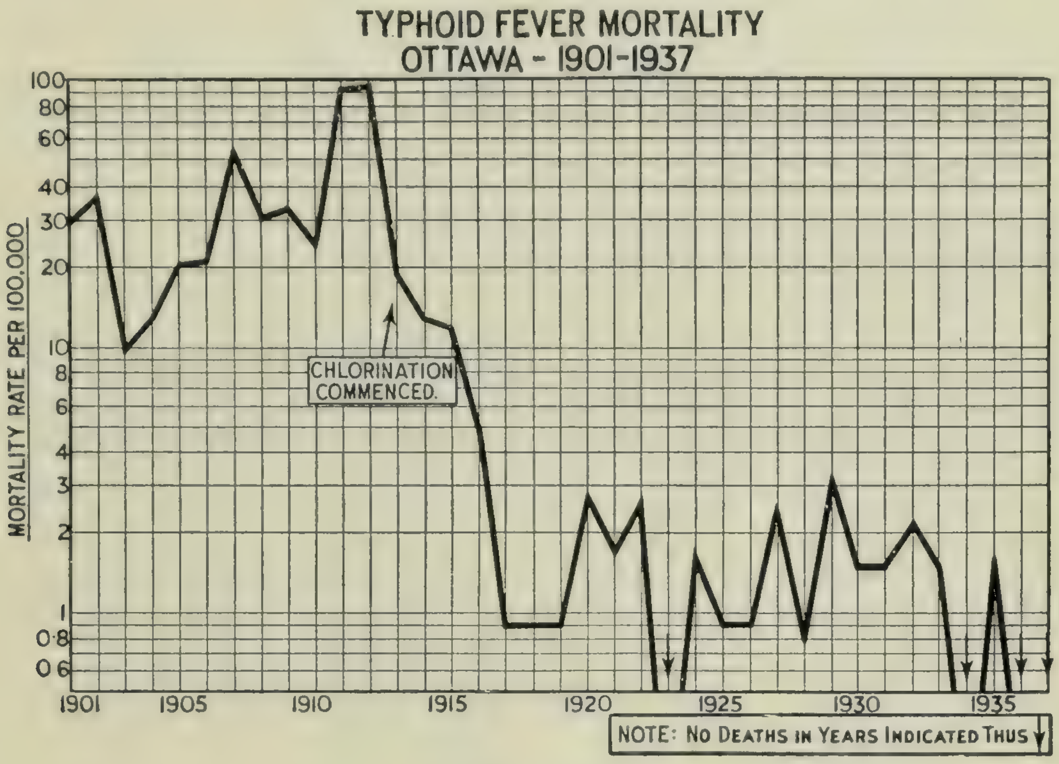


FIG. 64

After the epidemic year of 1911 and 1912 the river water was treated by chlorination. Apparently the water-supply was the main factor in typhoid fever. There is no record of any milk-borne epidemics. The general improvement in sanitation probably played a minor part in the reduction of typhoid.

In some parts of the world ozone (O_3) is added to the water to destroy bacteria. Sometimes very small plants, known as algae, give to natural water a very disagreeable taste. This can be overcome by the addition of copper sulphate ($CuSO_4$) in small amounts to the water in the settling basins.

8. The Composition of Water

Chemists are always interested in the composition of materials and a study of the composition of water will serve as an illustration of how the composition of any chemical compound may be determined.

(1) METHODS OF DETERMINING THE COMPOSITION OF ANY COMPOUND. I. *Analysis.* The *analysis* or decomposition of a compound tells us *what elements* are present in it. There are

two chief branches of analytical chemistry, *qualitative analysis* and *quantitative analysis.* The methods used in qualitative analysis enable chemists to tell what elements or radicals are present in any unknown sample. The procedures used in quantitative analysis give us the per cent of various elements or radicals in any compound or mixture.

2. *Synthesis.* Synthesis or combination is the building up of compounds from elements. When a chemist discovers by analysis what elements are present in a compound, he is always very anxious to synthesize the compound from these elements. If he is successful in this, then he has established the chemical composition of the compound under consideration.

(2) THE DECOMPOSITION OF WATER. Water can be decomposed by electricity, using a suitable apparatus, into hydrogen and oxygen. When this is done in a quantitative manner, using the Hofmann apparatus (see page 28), it is found that exactly twice as much hydrogen *by volume* than oxygen is produced.

(3) SYNTHESIS OF WATER. 1. *By Volume.* By means of an apparatus called a *eudiometer* water can be synthesized from its constituent elements. A eudiometer consists of a graduated glass tube about thirty inches in length, closed at one end, and it has two pieces of platinum wire fused through opposite sides of the wall near the closed end. The two pieces of wire are about two to three millimetres apart and this distance is known as the spark gap.

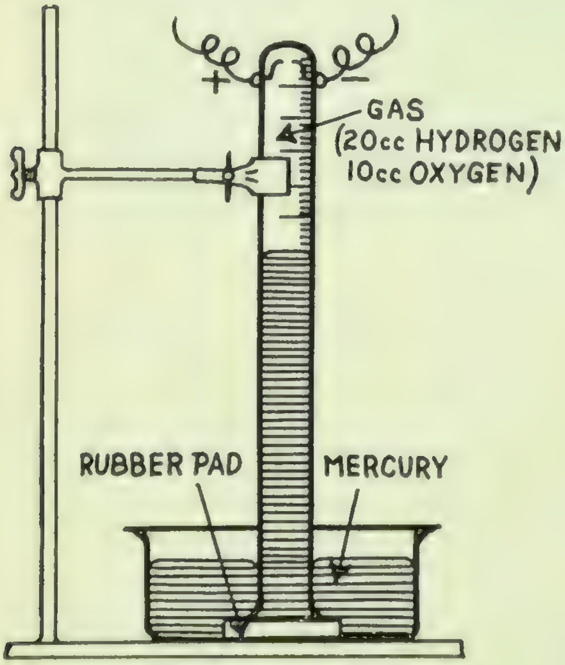


FIG. 65—A EUDIOMETER

The eudiometer is filled with mercury and inverted in a dish of mercury. Oxygen is then introduced into the apparatus and the volume is measured by means of the graduations on the tube. Then hydrogen is passed into the eudiometer and its volume is also measured. When certain precautions have been taken, an electric spark is passed between the ends of the platinum wires, and oxygen and hydrogen combine in the tube almost noiselessly. The steam produced condenses to a small drop of water. If the oxygen and hydrogen were used in exactly the proportion of one volume of the former to two of the latter, the mercury would rise to the top of the tube. If these two gases were mixed in the apparatus in any other proportions, the excess of one or the other, as the case might be, would be left uncombined at the end of the experiment.

If the above experiment is repeated *at the temperature of steam*, it is found that the following result is obtained:

2 vols. hydrogen + 1 vol. oxygen ⟶ 2 vols. steam

This is an example of *Gay-Lussac's Law of Combining Volumes*, which states that *the volumes of gases used andproduced in chemical changes can always be represented by a ratio of small whole numbers*. This law was discovered by Gay-Lussac in 1809. A few other examples of this law are given below:

1 vol. nitrogen + 3 vols. hydrogen ⟶ 2 vols. ammonia

1 vol. hydrogen + 1 vol. chlorine ⟶ 2 vols. hydrogen chloride

2 vols. carbon monoxide + 1 vol. oxygen ⟶ 2 vols. of carbon dioxide

The following mathematical examples will illustrate the use of this law.

EXAMPLE I.

A mixture of 15 c.c. of oxygen and 40 c.c. of hydrogen was exploded in a eudiometer at the temperature of steam.

Find: (a) What volume of steam was produced?
(b) What other gas was mixed with it?
(c) What is the volume of this other gas?

2 vols. hydrogen + 1 vol. oxygen ⟶ 2 vols. steam

30 c.c. + 15 c.c. ⟶ 30 c.c.

According to Gay-Lussac's law 15 c.c. of oxygen combines with 30 c.c. of hydrogen to produce 30 c.c. of steam. Since the mixture contained 40 c.c. of hydrogen at the start there would be 10 c.c. of this gas left at the end with the 30 c.c. of steam.

EXAMPLE 2.

A mixture of 1200 c.c. of hydrogen and 500 c.c. of nitrogen was treated in such a way to produce ammonia.

Find: (a) What volume of ammonia was formed?

(b) What gas was mixed with the ammonia and what was its volume?

3 vols. hydrogen + 1 vol. nitrogen ⟶ 2 vols. ammonia

1200 c.c. + 400 c.c. ⟶ 800 c.c.

It is evident from the above equation that 800 c.c. of ammonia was produced and that it would be mixed with 100 c.c. of nitrogen.

2. *By Weight.* As the exact measurement of pure gases is very difficult, roundabout methods are often devised by chemists to avoid such measurements. The reduction of copper oxide by hydrogen can be used to synthesize water and to study its composition by weight. A French chemist, Dumas, did this experiment on a large scale in 1842 and it is sometimes known as *Dumas' experiment.* The details of this experiment, somewhat simplified, are as follows:

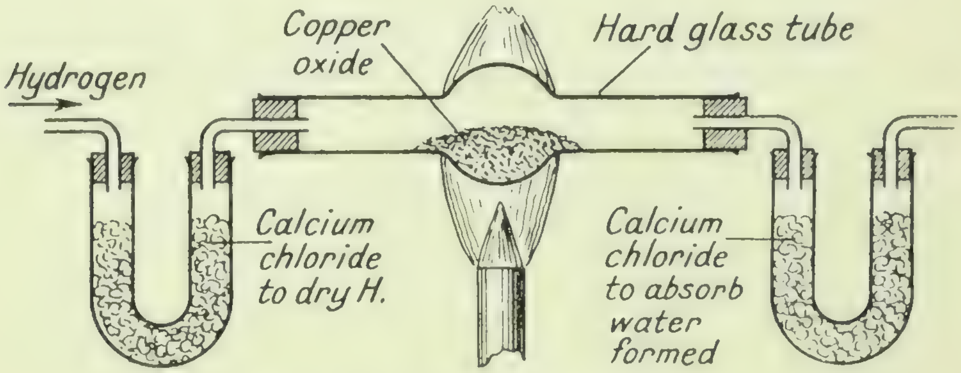

Copper oxide
Hard glass tube
Hydrogen
Calcium chloride to dry H.
Calcium chloride to absorb water formed

FIG. 66—DUMAS' EXPERIMENT
The Synthesis of water by weight.

(1) Weigh some copper oxide.
(2) Pass *dry* hydrogen over the copper oxide while hot.
(3) Collect the water formed in a weighed calcium chloride drying tube.
(4) Weigh the copper left in the tube.
(5) Weigh the drying tube at the end of the experiment.
(6) From the data obtained calculate the per cent of oxygen and hydrogen in water.

In a typical experiment the figures were:

Weight of copper oxide + tube *before* expt. = 314.58 g.
" " copper " " *after* " = 294.22 g.

Weight of oxygen = 20.36 g.

Weight of calcium chloride tube *after* expt. = 429.27 g.
" " " " " *before* " = 406.36 g.

Weight of water = 22.91 g.

$$\% \text{ oxygen in water} = \frac{20.36}{22.91} \times 100 = 88.80$$

$$\% \text{ hydrogen } '' \quad '' = 100 - 88.8 = 11.20$$

In 1895 Morley, an American chemist, determined the composition of water with very great care and accuracy. He found that 2.016 grams of hydrogen combines with exactly 16 grams of oxygen.

9. Uses of Water

Water is the most useful of all liquids and some of its more important uses are tabulated below:

(1) Drinking
(2) Washing
(3) Fire protection
(4) Steam power
(5) Navigation
(6) Heating systems
(7) Hydro-electric
(8) Solvents
(9) In plant life.

EXERCISES

1. Why is rain water the purest form of natural water?
2. How would you destroy bacteria in water?
3. What two classes of impurities are found in natural water?
4. (a) Is it necessary to remove all impurities from water in order to make it safe for drinking?
   (b) If not, how can we make it safe for drinking?
5. (a) What is the difference between *filtration* and *distillation?*
   (b) Describe each, mentioning the kinds of impurities separated.
6. How would you prove that a certain colourless liquid was water?
7. In what measurements is water selected as a standard?
8. Compare the properties of water with the properties of the elements that compose it.
9. 18 c.c. of pure oxygen is added to 26 c.c. of pure hydrogen in a eudiometer over mercury. A spark is passed through the mixture. Will any gas be left uncombined? If so, what will it be, and what will it measure? Why did it not all combine?
10. Into what two classes can the methods for determining the composition of water be divided?
11. What is the difference between qualitative and quantitative analysis?
12. Dumas obtained the following results in one of his experiments:
    Wt. of cupric oxide and tube before expt. = 673.28 g.
    Wt. of copper and tube after expt. = 613.49 g.
    Wt. of drying tube before expt. = 931.49 g.
    Wt. of drying tube after expt. = 998.77 g.
    Calculate from this data the percentage composition of water.

CHAPTER XV

MOLECULAR WEIGHTS

1. Avogadro's Hypothesis

In 1811 an Italian chemist, Avogadro, proposed the hypothesis that *equal volumes of all gases, under the same conditions of temperature and pressure, contain equal numbers of molecules.* Thus, if one litre of hydrogen, at S.T.P., contains X molecules, then one litre of oxygen, or nitrogen, or carbon dioxide, or of any other gas, at S.T.P., contains X molecules. (It has been found that $X = 2.7 \times 10^{22}$.) Avogadro's hypothesis has been very important in the development of chemical theory and it has also given chemists a method of determining the relative weights of the molecules of different gases.

2. The Fundamental Method for Determining Molecular Weights

It is impossible to determine the actual weights of gas molecules by experiment but we can determine their relative weights by means of Avogadro's hypothesis. The chief steps of this method are as follows:

(1) *Determination of the weight of one litre of a number of gases.* This can be done in the laboratory by means of very careful experiments and the results of this work for a few gases are given in table 8.

(2) Let X equal the number of molecules in one litre of oxygen and therefore, according to Avogadro's hypothesis, one litre of any other gas, under the same conditions of temperature and pressure, contains X molecules.

(3) Calculate the *actual weight* of various gas molecules. A few calculations are shown below.

(a) *Hydrogen*

X molecules of hydrogen weigh .09 g.

1 molecule of hydrogen weighs $\frac{.09}{X}$ g.

(b) *Oxygen*

X molecules of oxygen weigh 1.43 g.

1 molecule of oxygen weighs $\frac{1.43}{X}$ g.

(c) *Nitrogen*

X molecules of nitrogen weigh 1.25 g.

1 molecule of nitrogen weighs $\frac{1.25}{X}$ g.

(d) *Carbon dioxide*

X molecules of carbon dioxide weigh 1.98 g.

1 molecule of carbon dioxide weighs $\frac{1.98}{X}$ g.

(4) *Compare the actual weights of the various gas molecules with some standard.* Let us select $\frac{1}{32}$ of the weight of the oxygen molecule as the standard for this comparison.

$$\textit{Standard} = \frac{1}{32} \text{ of } \frac{1.43}{X} \text{ g.} = \frac{1.43}{32X} \text{ g.}$$

To secure the relative weights of the gas molecules under consideration, we divide their actual weights by the standard. A few calculations are shown below.

$$\frac{\text{Wt. of oxygen molecule}}{\text{Wt. of the standard}} = \frac{\frac{1.43}{X}}{\frac{1.43}{32X}} = 32$$

$$\frac{\text{Wt. of hydrogen molecule}}{\text{Wt. of the standard}} = \frac{\frac{.09}{X}}{\frac{1.43}{32X}} = 2$$

$$\frac{\text{Wt. of nitrogen molecule}}{\text{Wt. of the standard}} = \frac{\frac{1.25}{X}}{\frac{1.43}{32X}} = 28$$

$$\frac{\text{Wt. of carbon dioxide molecule}}{\text{Wt. of standard}} = \frac{\frac{1.98}{X}}{\frac{1.43}{32X}} = 44$$

From the above calculations we have obtained *numbers* which give us the relative weights of molecules compared to 1/32 of the weight of the oxygen molecule. These numbers are known as *molecular weights.* Thus 32 is the molecular weight of oxygen, 2 is the molecular weight of hydrogen, 28 is the molecular weight of nitrogen and 44 is the relative weight of a carbon dioxide molecule. (Some of the numbers used in the above discussion will not appear quite accurate. This is due to the fact that we do not calculate out to many places of decimals. Thus, the weight of one litre of hydrogen is really 0.0898 g., and not 0.09, as we have used it.)

TABLE 8—THE DENSITIES AND MOLECULAR WEIGHTS OF SOME GASES

Gas	Wt. of 1 litre at S.T.P.	Wt. of 22.4 litres at S.T.P.	Mol. Wt.
Acetylene (C_2H_2)	1.17	26 g.	26
Air	1.29	29 g.	29
Ammonia (NH_3)	0.77	17 g.	17
Carbon dioxide (CO_2)	1.98	44 g.	44
Carbon monoxide (CO)	1.25	28 g.	28
Chlorine (Cl_2)	3.21	71 g.	71
Hydrogen (H_2)	0.09	2 g.	2
Hydrogen sulphide (H_2S)	1.54	34 g.	34
Methane (CH_4)	0.72	16 g.	16
Nitric oxide (NO)	1.34	30 g.	30
Nitrogen (N_2)	1.25	28 g.	28
Nitrous oxide (N_2O)	1.98	44 g.	44
Oxygen (O_2)	1.43	32 g.	32
Sulphur dioxide (SO_2)	2.93	64 g.	64
Water (steam)	0.80	18 g.	18

(5) *Gram molecular weight* (*G.M.W.*). If the numbers obtained in the previous section are expressed as *grams*, then we have a set of values which are known as gram molecular weights. The gram molecular weight of a substance is often abbreviated as G.M.W. Now let us calculate what volume a few of the gram molecular weights of some common gases would occupy at S.T.P.

(a) *Hydrogen*

.09 grams of hydrogen occupies 1 litre at S.T.P.

2 grams of hydrogen occupies $\frac{1}{.09} \times 2 = 22.4$ litres at S.T.P.

(b) *Oxygen*

1.43 grams of oxygen occupies 1 litre at S.T.P.

32 grams of oxygen occupies $\frac{1}{1.43} \times 32 = 22.4$ litres at S.T.P.

(c) *Nitrogen*

1.25 grams of nitrogen occupies 1 litre at S.T.P.

28 grams of nitrogen occupies $\frac{1}{1.25} \times 28 = 22.4$ litres at S.T.P.

(d) *Carbon dioxide*

1.98 grams of carbon dioxide occupies 1 litre at S.T.P.

44 grams of carbon dioxide occupies $\frac{1}{1.98} \times 44 = 22.4$ litres at S.T.P.

Calculations of the above type have been done for all the known gases and the answer is always 22.4 litres at S.T.P. Some careful thought will show that, due to Avogadro's hypothesis, the answer should be the same for any gas. In conclusion, we may say that *the weight in grams of 22.4 litres of any gas, at S.T.P., is numerically equal to the molecular weight of the gas.* The data given in the table on page 112 will help to illustrate this fact.

(6) *The Gram molecular volume (G.M.V.). The value, 22.4 litres, is called the gram molecular volume of a gas because the weight in grams of this volume of any gas, at S.T.P., is numerically equal to its molecular weight.* It is often abbreviated to *G.M.V.*

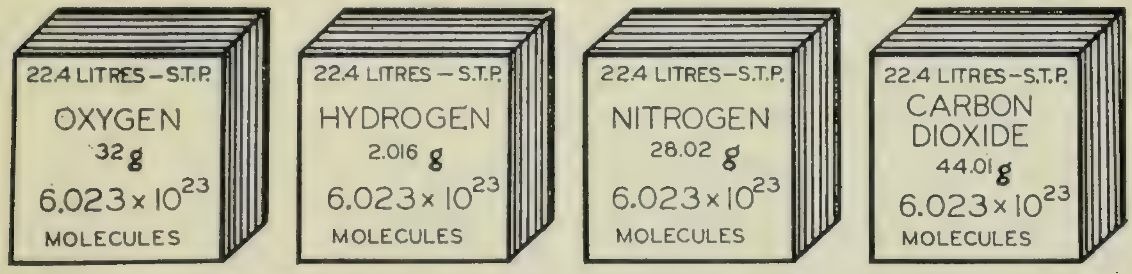


Fig. 67—The Weight of 22.4 Litres of Various Gases

The molecular weight of a gas, then, can be found by determining the weight in grams of 22.4 litres of that gas at S.T.P.

Example 1

A litre of gas under standard conditions weighs 1.50 g. What is the molecular weight of the compound?

1 litre of the compound weighs 1.50 g. at S.T.P.
22.4 " " " " " $1.50 \times 22.4 = 33.60$ g.
Thus the molecular weight = *33.60.*

EXAMPLE 2

A sample of gas measuring 240 c.c. at 20° C. and 740 mm. weighs 0.215 g. What is its molecular weight?

First the volume must be changed to S.T.P.

$$240 \times \frac{273}{293} \times \frac{740}{760} = 217.8 \text{ c.c.}$$

Now 217.8 c.c. at S.T.P. weighs 0.215 g.

$$1 \text{ c.c.} \quad '' \quad '' \quad '' \quad \frac{0.215}{217.8} \text{ g.}$$

$$1000 \text{ c.c. (1 litre)} \quad '' \quad \frac{0.215}{217.8} \times 1000 \text{ g.}$$

$$22.4 \text{ litres at S.T.P.} \quad '' \quad \frac{0.215}{217.8} \times 1000 \times 22.4 = 22.11 \text{ g.}$$

Hence the molecular weight = *22.11.*

There are many indirect methods of determining molecular weights, including those of liquids and dissolved solids, but these are beyond the scope of this book.

The density of any gas compared with air, may be determined by comparing the weight of 22.4 litres of that gas, which is its molecular weight expressed in grams, with the weight of 22.4 litres of air, which is approximately 29 grams. Thus, the density of sulphur dioxide compared with air is 2.2, that is $\frac{64}{29}$.

3. Avogadro's Number

The *number* of molecules in 1 gram molecular weight (1 mole) of any substance is always the same, no matter whether the substance is a gas or not. This number is 6.02×10^{23} at S.T.P. and is called Avogadro's number. It is a constant and the letter N is often used to represent it.

The value of this constant has been determined in many different ways and the results always agree very closely.

EXERCISES

1. (a) State Avogadro's hypothesis.
   (b) Outline carefully the fundamental method for determining molecular weights.
2. 1 c.c. of a gas weighs 0.00286 g. at S.T.P. What is its molecular weight?

3. If 200 c.c. of a gaseous compound at 20° C. and 700 mm. weighs 0.2730 g., calculate the molecular weight of the compound.
4. (a) What is the G.M.W. of a substance?
   (b) What is the G.M.V.? What is its chief use?
5. One litre of a gas at 273° C. and 741 mm. weighs 8.60 g. Calculate its molecular weight.
6. If 1 litre of a gas at S.T.P. weighs 2.927 g., what is the G.M.W. of the gas?
7. Find the weight of 3 litres of carbon dioxide, CO_2, at S.T.P.
8. Find the volume occupied by 6 g. of hydrogen at S.T.P.
9. Calculate the molecular weight of a gas, 2 litres of which weighs 3 g. at S.T.P.
10. What is the weight of 10 litres of nitrogen at S.T.P.?
11. 12 g. of oxygen are collected in an experiment. What would be the volume of this gas at S.T.P.?
12. A balloon weighing 300 g. with a capacity of 5,000 litres is filled with hydrogen at S.T.P. Find the weight of the filled balloon.
13. What is the weight of 4 litres of ammonia, NH_3, at S.T.P.?
14. 340 c.c. of a gas weighs 0.4 g. at S.T.P. What is the molecular weight of the gas?
15. What is the weight of 150 c.c. of oxygen at S.T.P.?
16. Find the volume of hydrogen which weighs 15 g. at S.T.P.?

CHAPTER XVI

SOLUTIONS

1. What is a Solution?

When salt is stirred into water the white solid disappears completely. If we heat this mixture until all the water has been driven off, we observe that the salt is left behind and that it has the same properties which it had at the beginning. It has not been changed into any other substance by the water. *The dissolving of the salt in the water is a physical change.* The chemist describes the above facts by saying that the salt *dissolves* in the water and he calls the resulting liquid a salt *solution*. The substance which does the dissolving is called the *solvent* (water), and the substance which is dissolved is called the *solute* (salt).

If a coloured solute, such as potassium chromate, is stirred in water, it is observed that the yellow colour of the solute is evenly distributed throughout the solvent. This fact proves that the solution is *homogeneous* (even) and a solution may be *defined as a homogeneous sample of matter of variable composition*.

If there is only a small amount of the solute in a solution, it is known as a *dilute* solution; if much solute has been dissolved, it is called a *concentrated* solution. For example, honey is a concentrated solution of sugar; the sap of a maple tree is a dilute solution of sugar.

It is interesting to compare solutions with mixtures and compounds. Mixtures are *heterogeneous*, which means that they are not even throughout their entire mass, while solutions and compounds are *homogeneous*. Mixtures can be prepared in various proportions and the same is true for many solutions. Compounds, on the other hand, always possess a definite composition. It is apparent, then, that solutions stand mid-way between mixtures and compounds in certain outstanding characteristics. The following table summarizes these facts.

Mixtures	Solutions	Compounds
Heterogeneous Variable Composition	Homogeneous Variable Composition	Homogeneous Definite Composition

2. Suspensions and Emulsions

When finely powdered sand or clay (insoluble in water) is well shaken or stirred in water, a milky or muddy-looking (*turbid*) liquid is obtained. This liquid is known as a *suspension.* The solid is not dissolved, and if the mixture stands quietly for a time the solid slowly settles to the bottom of the vessel, leaving the liquid clear. The solid can, as a rule, be removed more rapidly by passing the mixture through filter paper. *The solute in a true solution*, on the other hand, *never settles out*, no matter how long we wait, nor can it be filtered out.

Milk owes its cloudy, white appearance chiefly to droplets of oily matter, which reflect much light from their surfaces. They pass easily through filter paper, but when milk is allowed to stand, these particles rise slowly to the top as cream, being lighter than the water in which they are not dissolved but suspended. A mixture of two *liquids* of this nature is called an *emulsion.*

3. Solvents

Water is by far the commonest and most useful of all solvents. Many substances dissolve in it easily. The fact that many materials, such as sulphur and sand, do not, enables us to separate the components of a mixture containing a soluble and an insoluble substance.

Many substances, such as fat, paraffin, petroleum, tar, rubber, cotton, paper, shellac and so forth, do not dissolve in water. However, fats dissolve readily in ether, in carbon disulphide (CS_2), in carbon tetrachloride (CCl_4) and in chloroform ($CHCl_3$). For this reason these liquids remove grease which has stained cloth. Paraffin, petroleum, and tar dissolve in gasoline. Alcohol (C_2H_5OH) dissolves shellac and use is made of this fact in the production of varnish. Carbon disulphide is a good solvent for rubber and sulphur, and turpentine is an excellent solvent for paints.

4. Types of Solution

There are a number of types of solutions other than the solution of a solid in a liquid. Since a solution is a homogeneous sample of matter of variable composition, it is evident that solutions are not limited to this one group of mixtures. In theory, it should be possible to produce the following types of solutions, which are different in the physical state of the solutes and solvents.

(1) Gases in gases.
(2) Liquids in gases.
(3) Solids in gases.
(4) Gases in liquids.
(5) Liquids in liquids.
(6) Solids in liquids.
(7) Gases in solids.
(8) Liquids in solids.
(9) Solids in solids.

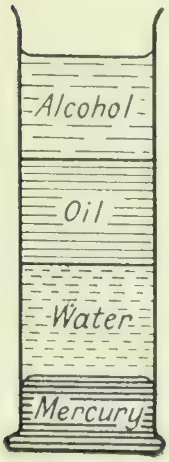


FIG. 68
NON-MISCIBLE LIQUIDS

Every gas freely mixes with every other gas in all proportions, and such a mixture may be thought of as a solution of one gas in another. It is hard to think of a solid or a liquid dissolving in a gas to produce a homogeneous mixture, although, under special conditions, such mixtures have been observed. Gases and solids dissolve in liquids. One liquid often dissolves in another or, in other words, the two liquids mix. Such liquids are said to be *miscible.* Liquids such as oil and water which do not mix are said to be *non-miscible* (see Fig. 68). One solid sometimes dissolves in another solid, as in the case of alloys, and we also have examples of gases and of liquids dissolved in solids. The most familiar types of solutions are those in which a liquid is the solvent, and a gas, a second liquid, or a solid is the solute.

5. Saturation

(a) SATURATED SOLUTIONS. Let us suppose that a large crystal of some soluble substance, such as cane sugar, $C_{12}H_{22}O_{11}$, is placed in the bottom of a beaker filled with water. According to the molecular theory there are *two tendencies* at work in such a case:

1. There is the tendency of the sugar molecules to go into solution.
2. There is the tendency of the sugar molecules to return to the crystal.

Let S_1 = *speed or velocity* of the first tendency, where *speed* means the quantity of material going into solution per unit of time.
Let S_2 = speed or velocity of the second tendency.
In time, $S_1 = S_2$, and then we have a *condition* or *state of affairs* called *equilibrium.* Since the dissolving of sugar in water is a physical change, it is known as *physical equilibrium.* This condition is called *saturation.* Thus, *a saturated solution* can be defined as *one which is in equilibrium with the undissolved solute at a given temperature.* It should be remembered that the

equilibrium is not between solute and solvent, but between *solute in solution* and *solute still in the solid form.*

The weight of the solid that will completely saturate a definite weight of a given solvent at a given temperature is called the *solubility* of the solid in that solvent. It is usually defined thus: *the solubility of a solid at a given temperature is the weight in grams of the solid that will saturate 100 grams of the solvent.* (See Appendix II, page 526).

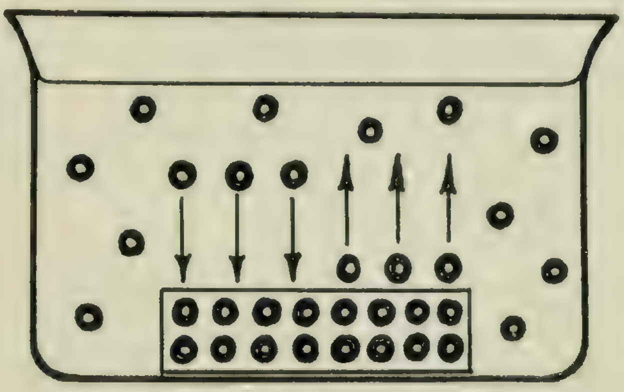


Fig. 69—Equilibrium Between a Solid and a Saturated Solution

(b) Unsaturated Solutions. Those solutions, in which equilibrium has not been reached and more solute goes into solution at a given temperature, are called *unsaturated.*

(c) Supersaturated Solutions. A hot solvent usually dissolves much more of a given solid than does the same solvent when cold. A solvent saturated at a high temperature usually deposits the excess of the solute in the form of crystals as the temperature falls, remaining saturated at all times. Sometimes, however, the crystals do not form as the solution cools, especially if no crystals are present when it starts to cool, and if it is not disturbed in any way. The solution, when cool, will then contain more of the solute than does a saturated solution at a given temperature. Such a solution is said to be supersaturated. If even a very small crystal of the solute is dropped into a supersaturated solution, the excess of solute at once crystallizes out, leaving the solution saturated. Some jellies are supersaturated solutions and often deposit the excess of

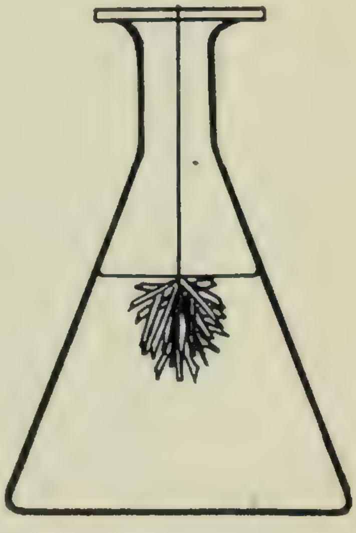


Fig. 70—Crystallization of a Supersaturated Solution

sugar crystals. If heated until all crystals have dissolved and then carefully cooled, supersaturation may be again secured. The hydrates of sodium sulphate (Glauber's salt $Na_2SO_4 . 10H_2O$) and of sodium thiosulphate (photographers' "hypo" $Na_2S_2O_3 . 5H_2O$) give solutions of this kind in water.

A supersaturated solution can be distinguished from a saturated or an unsaturated solution in a very simple way. The addition of a small crystal of the solute to a supersaturated solution usually brings about crystallization, whereas in the case of a saturated solution the crystal remains undissolved at the bottom of the vessel. Of course, the crystal dissolves when added to an unsaturated solution.

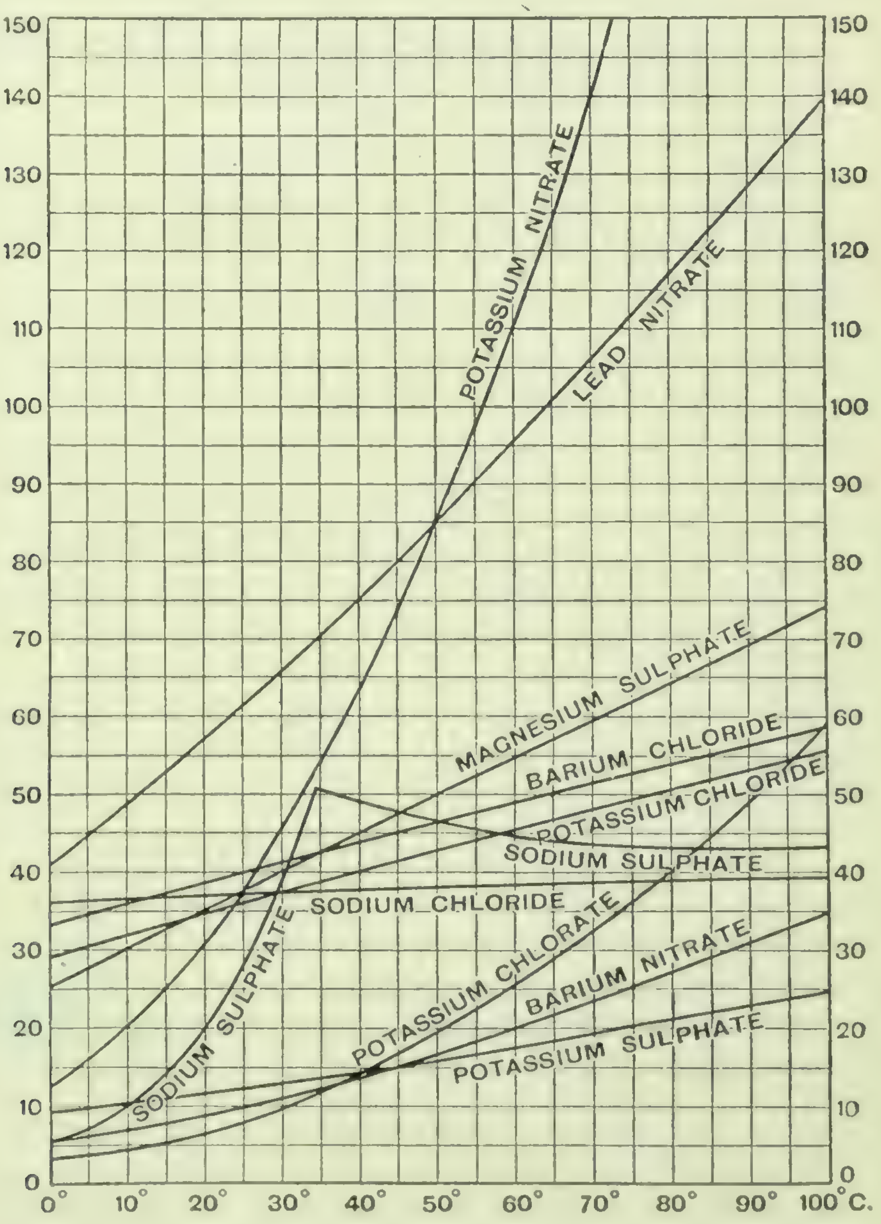


FIG. 71—SOLUBILITY CURVES FOR A FEW COMMON SUBSTANCES IN WATER

EARTH'S ANGEL.

6. Effect of Temperature Upon Solubility

The quantity of a substance which will dissolve in 100 grams of a given solvent depends very largely upon the temperature. As a rule the solubility of solids in liquids increases with a rise in temperature. Fig. 71 shows the solubility curves for a few common substances in water. A study of this illustration shows that 100 g. of water dissolve 13 g. of potassium nitrate at 0° C. and 85 g. at 50° C. The increase in solubility is, in this case, very great. On the other hand, the same quantity of water will dissolve 35.6 g. of sodium chloride at 0° C. and 39 g. at 100° C. The difference is observed at once when the curves are examined. The line representing the solubility of sodium chloride rises slightly between 0° and 100°, while that of potassium nitrate goes up very quickly.

There are a few solids which are less soluble in hot water than in cold water. For example, the solubility of slaked lime, calcium hydroxide, $Ca(OH)_2$, which is used to make limewater, is 0.175 g. at 20° C. and 0.078 g. at 100° C.

7. Factors Affecting Solubility

(1) THE NATURE OF THE SOLUTE. Every substance has its own definite solubility at a certain temperature in some liquid. All materials, whether solids, liquids, or gases, may be considered to be soluble *to some extent* in every liquid. However, in many cases the solubility is too small to be measured.

(2) THE NATURE OF THE SOLVENT. Various solvents differ greatly in their ability to dissolve materials. Sugar, for example, is very soluble in water, but only slightly soluble in alcohol.

(3) THE TEMPERATURE. This has already been considered in the last section.

(4) PRESSURE. Pressure has no appreciable effect upon the solubility of solids in liquids. It has, however, a marked influence upon the solubility of a gas in a liquid. When we increase the pressure upon a gas, which is above a liquid, much more gas is forced into the solution. There is a law, known as Henry's Law, regarding this. The statement of the law is as follows: *The weight of a gas (if that gas is not too soluble) which dissolves in a definite volume of a liquid is directly proportional to the pressure which the gas exerts above the liquid at a constant temperature.* If the pressure is doubled, the weight of the gas going into solution is also doubled. Under high pressure large

quantities of many gases can be forced into solution. When the pressure is removed, most of the gas escapes, causing the liquid to foam or effervesce. Soda water is a good example of a liquid holding a gas (carbon dioxide) in solution under pressure, the usual pressure being about 150 lbs. per sq. in. (10 times that of the air).

8. The Effect of Solutes Upon the Freezing and Boiling Points of Solvents

(1) THE EFFECT UPON THE FREEZING POINT (F.P.). The freezing point of a solvent is *lowered* upon the addition of a solute. Chemists have discovered that there is a rule or law regarding this phenomenon. This rule states *that when 1 gram molecular weight of a substance is dissolved in 1000 grams of water, the resulting solution freezes at* $-1.86°$ C. For example, the gram molecular weight of cane sugar is 342 grams. This value is obtained from the formula of sugar and the atomic weights of the elements which make up that compound, as follows:

$$C_{12}H_{22}O_{11} = 12 \times 12 + 22 \times 1 + 11 \times 16 = 342$$
$$(C = 12,\ H = 1,\ O = 16).$$

If 342 grams of sugar is dissolved in 1000 g. of water, the solution does not freeze until the temperature drops to 1.86° C. below zero. The gram molecular weight of alcohol will do the same when dissolved in 1000 grams of water. The formula for alcohol (ethyl alcohol) is C_2H_6O and its molecular weight can be calculated as follows:

$$C_2H_6O = 2 \times 12 + 6 \times 1 + 1 \times 16 = 46$$

46 g. of alcohol in 1000 g. of water lowers f.p. 1.86° C.
460 g. of alcohol in 1000 g. of water lowers f.p. 18.6° C.
920 g. of alcohol in 1000 g. of water lowers f.p. 37.2° C.

From the above figures it is evident that the lowering of the F.P. of the solvent is directly proportional to the number of molecules of solute present. Thus, 460 g. of alcohol contain ten times as many molecules as 46 g. and the lowering of the F.P. is 18.6° C. which is, of course, ten times the lowering when 46 g. of alcohol is used as the solute. A practical application of this phenomenon is the use of alcohol and other liquids as anti-freeze for the radiators of automobiles.

(2) THE EFFECT UPON BOILING POINT (B.P.). The boiling point of a solvent is *raised* by the addition of a solute. The

rule, in this case, is that 1 gram molecular weight dissolved in 1000 grams of water, raises the boiling point exactly 0.52° C.

(3) Exceptions. It has been found, when an acid, base or salt is added to water, that the values for the elevation of the boiling point and the lowering of the freezing point are greater than those for other substances. This would suggest that, in some way, acids, bases and salts must produce more dissolved particles, when placed in a solvent, than other materials. This fact will be considered again when we study the theory of ionization.

9. Crystallization

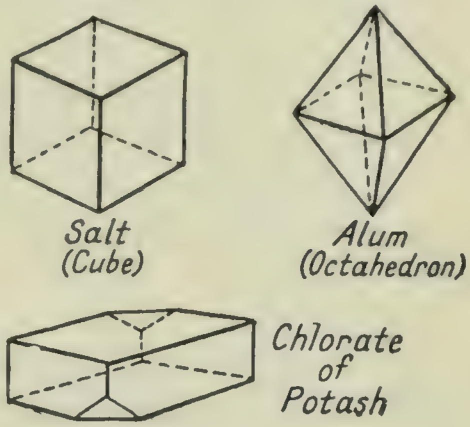


Fig. 72—Crystals

Crystallization is the separation of a solute from a solution in the form of crystals. Crystals are solids, the units of which possess definite shapes. They are bounded by plane surfaces which, in a given type, form definite angles to one another. Various types of crystals exist, such as cubes, rhomboids, octahedrons, monoclinic and so forth. For example, salt crystals are cubic, alum crystals are octahedron and sulphur can be prepared in both rhombic and monoclinic forms. The study of crystals is an interesting one and the subject matter of that branch of science is called *crystallography*.

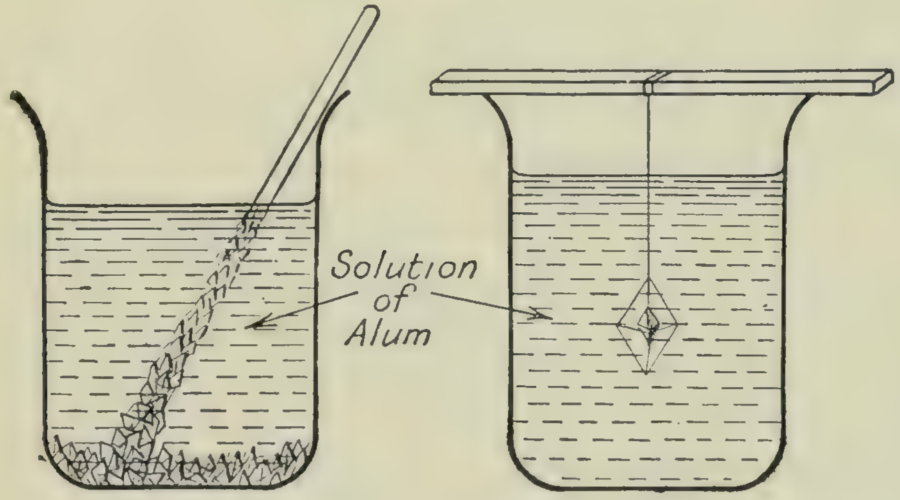


Fig. 73—The Way to Form Alum Crystals

Dissolve as much alum as possible in a little warm water. Pour off the clear liquid and place a wooden splint in the solution. The next day, remove one crystal of alum from the splint and pour the clear liquid into another beaker. Suspend the single crystal in this liquid by a thread. The small crystal in the right-hand beaker will gradually grow to form a large crystal.

The methods of obtaining crystals are as follows:

(1) *From a supersaturated solution.* A saturated solution of the substance at a high temperature is prepared and allowed to cool slowly without being disturbed. If the solubility of the material is much less at room temperature, crystals will form when a small crystal of the solute is added to the solution.

(2) *From a saturated solution.* The slow evaporation of a saturated solution, without disturbance, usually results in the formation of large, well-shaped crystals. Rapid boiling away of the liquid, on the other hand, produces a crust of very small and, as a rule, poorly formed crystals.

(3) *Freezing of liquids.* Crystals may also be formed, as in the case of ice, by the freezing of liquids.

If a solid does not possess crystalline form it is known as *amorphous.* Glue and glass are examples of such materials.

10. Hydrates

Often *certain* crystals, although carefully dried, are found to contain a definite proportion of water, chemically combined. This water is called *water of hydration* or water of crystallization, and the compounds containing it are called *hydrates.* Hydrated copper sulphate or blue stone is a good example of a hydrate. On heating, this substance gives off its water of hydration, turning from a blue crystalline solid to a white powder.

$$\underset{\text{(hydrated copper sulphate)}}{CuSO_4.5H_2O} + \text{heat} \longrightarrow \underset{\text{(anhydrous copper sulphate)}}{CuSO_4} + 5H_2O$$

The loss of water of crystallization is known as *dehydration.* When water is added to anhydrous copper sulphate, five molecules of water combine with each molecule of copper sulphate to form molecules of blue hydrated copper sulphate.

$$CuSO_4 + 5\ H_2O \longrightarrow CuSO_4.5H_2O$$

Because of this colour change on hydration, anhydrous copper sulphate may be used as a reagent in making a *chemical test* for water. The process of taking up water of crystallization is known as *hydration.*

It will be observed that the formula for hydrated copper sulphate is written $CuSO_4.5H_2O$. The dot before the $5H_2O$ means that five molecules of water have combined with one molecule of anhydrous copper sulphate to form one molecule of a single substance, hydrated copper sulphate, which is composed of both $CuSO_4$ and H_2O in the proportions indicated in the formula. All formulas of hydrates show the number of molecules of water in the hydrate for each molecule of the anhydrous substance. The following table contains the names and formulas of a few common hydrates.

TABLE 9—SOME COMMON HYDRATES

Common Name	Chemical Name	Formula
Blue stone (Blue vitriol)	Copper sulphate	$CuSO_4 . 5H_2O$
Washing soda	Sodium carbonate	$Na_2CO_3 . 10H_2O$
Green vitriol	Ferrous sulphate	$FeSO_4 . 7H_2O$
Epsom salts	Magnesium sulphate	$MgSO_4 . 7H_2O$
Glauber's salt	Sodium sulphate	$Na_2SO_4 . 10H_2O$
Photographers' hypo.	Sodium thiosulphate	$Na_2S_2O_3 . 5H_2O$
Alum (potash alum)	Potassium aluminum sulphate	$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$

It is important to remember that although many crystals are hydrates, water is not necessary for the formation of crystals and many salts crystallize without combining with water. For example, common salt (sodium chloride) crystallizes from a water solution in the form of cubes and these crystals contain no water of crystallization. Diamonds, graphite, potassium chlorate ($KClO_3$), potassium sulphate (K_2SO_4), and potassium nitrate (KNO_3), are examples of crystalline materials which contain no water of crystallization.

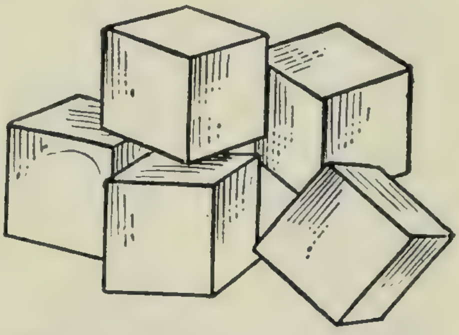


FIG. 74—SKETCH TO SHOW THE SHAPE TAKEN BY SALT CRYSTALS

11. Efflorescence and Deliquescence

(1) EFFLORESCENCE. Some hydrates lose their water of crystallization on exposure to dry air and often fall to powder. Such substances are called *efflorescent* (tending to become a powder) and the process is called *efflorescence.* For example, when washing soda crystals ($Na_2CO_3 . 10H_2O$) are exposed to the air, they change gradually to a dry powder. Glauber's salt ($Na_2SO_4 . 10H_2O$) is another good example of an efflorescent substance. They are said to *effloresce* when exposed to dry air.

(2) DELIQUESCENCE. Many solids absorb a film of moisture on their surfaces when exposed to the air. Some very soluble

substances, such as calcium chloride ($CaCl_2$), take up enough water from the air to become damp, and in some cases they dissolve. Because of this property, calcium chloride is sometimes used to settle dust on gravel or dirt roads. It is also used to dry gases or to absorb water in certain experiments. Materials which possess this property of absorbing moisture from the air are said to be *deliquescent* and the process is called *deliquescence.* Pure sodium chloride is not deliquescent, but ordinary table salt usually contains certain impurities, namely salts of calcium and magnesium, which are deliquescent. Thus, in wet weather common salt is usually deliquescent and this tendency is quite marked at the seashore. Sodium hydroxide, household lye, ($NaOH$) is also a good example of a deliquescent substance.

EXERCISES

1. Define the following terms and give one example of each: solution, solvent, solute, dilute solution and concentrated solution.
2. Give two ways of separating a mixture, consisting of a suspended solid and a liquid.
3. If you had a stain on your clothing consisting of: (a) grease; (b) honey; (c) honey and grease together; (d) varnish; what would you do in each case to remove the stain?
4. Make a list of the nine possible types of solution.
5. Discuss saturation carefully from the viewpoint of equilibrium.
6. What is meant by the phrase "solubility of a solid in a liquid"?
7. How can you tell experimentally whether a given solution is (a) saturated, (b) unsaturated, (c) supersaturated?
8. What is the difference between a solution and a compound?
9. Write a short note on the effect of temperature upon the solubility of a solid in a liquid.
10. Tabulate the chief factors affecting solubility.
11. (a) What effect does a solute have upon the freezing and boiling points of solvents?
    (b) What appears to be the cause of this effect?
    (c) Are there any exceptions to the rules which govern the effect stated in (a)?
12. (a) What is crystallization?
    (b) What are crystals?
    (c) Tabulate the methods of obtaining crystals.
13. (a) Define the following terms and give one example of each: water of hydration, hydrates, anhydrous, dehydration, hydration, efflorescence and deliquescence.
    (b) Write the names (common and chemical) and formulas for five hydrates.

CHAPTER XVII

DALTON'S ATOMIC THEORY

1. Introduction

Early in the study of chemistry it was found that matter could undergo two types of changes, *physical* and *chemical*. There are two chief kinds of chemical changes. These are *decomposition* (analysis) and *combination* (synthesis). Chemists have discovered several laws governing the *combination of substances by weight*. Two of these laws, the Law of Conservation of Mass and the Law of Definite Proportions, have already been considered in previous chapters. There are several other laws, dealing with the combination of materials by weight, but their study is beyond the scope of this book.

2. Dalton's Atomic Theory

The laws of chemical combination by weight tell us *how* the elements combine to form compounds. The question is, *why*

Courtesy of International Nickel Co. of Canada Ltd.

FIG. 75—JOHN DALTON (1766–1844)

A famous English schoolmaster and scientist. He made many discoveries, but his greatest contribution to chemistry was his development of the atomic theory.

do the elements always combine in the ways stated in the laws? The answer to this question was given us by an English schoolmaster, John Dalton, in 1808. He proposed his famous atomic theory or hypothesis which explained *why* the laws of chemical combination always held true. It is well to remember that a theory or hypothesis is a *mental picture*, or assumption, used to explain *laws* or *facts*.

Dalton's chief postulates were:

(1) The elements are made up of indivisible particles called atoms.

(2) All the atoms making up any one element are exactly alike and have the same weight; but the atoms of one element differ from those of any other element.

(3) The atoms can combine with other atoms and are held together by a force called *chemical affinity*. It is this union of atoms which produces chemical compounds.

(4) Atoms cannot be divided, and therefore, only whole atoms combine with each other.

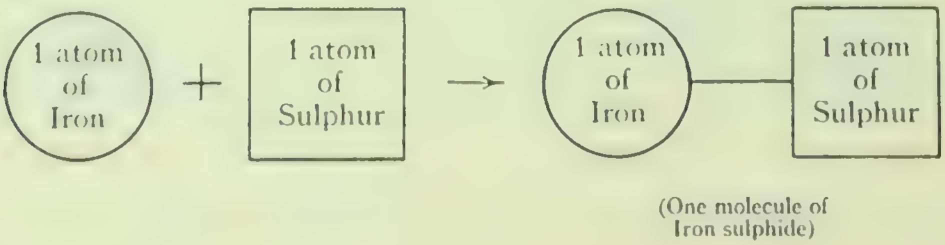
3. How Does Dalton's Theory Explain the Laws of Chemical Combination by Weight?

(1) The Law of Conservation of Mass. It is found in the laboratory that iron and sulphur will combine together when heated to form iron sulphide. According to the Law of Conservation of Mass, the weight of the iron sulphide produced is equal to the sum of the weights of iron and sulphur which combined. By experiment it has been found that 56 g. of iron will combine with 32 g. of sulphur to form 88 g. of iron sulphide.

Iron + Sulphur ⟶ Iron sulphide

56 g. 32 g. ⟶ 88 g.

According to the Atomic Theory one atom of iron combines with one atom of sulphur to produce one molecule of iron sulphide.



The theory states that all the atoms of any element have the same weight and hence all the iron atoms, which make up the sample of iron used in the experiment, have the same weight. Of course, sulphur atoms differ in weight from iron atoms but all sulphur atoms have the same weight. Since each molecule of iron sulphide is composed of one atom of iron and one atom of sulphur, the weight of all the iron sulphide molecules will be the same. Chemists suppose that in a chemical change the atoms are *redistributed*, but that none are produced or destroyed. The sum of the atoms of the substances which take part in a chemical reaction must equal the sum of the atoms in the products *since none are lost in the change.* This means that matter cannot be created or destroyed and hence this idea of atoms explains the Law of the Conservation of Mass.

(2) LAW OF DEFINITE PROPORTIONS. According to Dalton's theory, a compound is the result of the combination of atoms of different elements. For example, one atom of iron, which is indivisible and has a definite weight, will combine with one atom of sulphur, which is also indivisible and has a definite weight, to form a molecule of iron sulphide. The equation for this reaction is as follows:

$$\mathrm{Fe} + \mathrm{S} \longrightarrow \mathrm{FeS}$$

It is evident that a molecule of iron sulphide must consist of iron and sulphur combined in the proportions of the weights of their respective atoms, which are 56 and 32. Any sample of iron sulphide is made up of such molecules, and so the iron and sulphur in it must be present in the exact proportions in which they are present in each molecule, that is, 56 to 32. The same holds true for more complex molecules. Thus, the atomic theory explains the law of definite proportions.

4. To Prove that the Common Gases Contain Two Atoms per Molecule.

The pioneer chemists did not know the number of atoms in the molecules of various gases and it was not until Avogadro proposed his hypothesis, that *equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules*, that this important problem was solved.

(1) THE OXYGEN MOLECULE. *To prove that the oxygen molecule contains two atoms. By experiment* it has been found

that two volumes of hydrogen combine with one volume of oxygen to produce two volumes of steam.

Hydrogen + Oxygen → Steam
(2 litres) + (1 litre) → (2 litres)

Let X equal the number of molecules in one litre of oxygen; therefore, according to Avogadro's hypothesis, two litres of hydrogen would contain 2X molecules of hydrogen. The two litres of steam produced would also contain 2X molecules of steam, and so we can set up the following equation:

Hydrogen + Oxygen → Steam
(2X molecules) (X molecules) (2X molecules)

It is evident that one molecule of steam must contain *at least* one atom of oxygen. One molecule of steam might contain more than one atom of oxygen but we shall assume that it contains only one atom of oxygen. Starting from this assumption and making use of the information obtained above, we can develop the following relationships:

1 molecule of steam must contain at least 1 atom of oxygen
2X molecules " " " " " 2X atoms "

These 2X atoms of oxygen come from the X molecules of oxygen contained in the 1 litre of oxygen.

Hence we have the following:

X molecules of oxygen contain 2X atoms of oxygen.

1 molecule of oxygen contains $\frac{2X}{X}$ = *2 atoms* of oxygen.

All chemical reactions of oxygen can be explained by assuming that the molecule of oxygen contains two atoms; hence, experience tends to confirm the above proof.

(2) THE HYDROGEN MOLECULE. *To prove that the hydrogen molecule contains two atoms.* By experiment it is found that one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrogen chloride.

Hydrogen + Chlorine → Hydrogen chloride
(1 litre) (1 litre) (2 litres)

Let X equal the number of hydrogen molecules in one litre of hydrogen; therefore, according to Avogadro's hypothesis, one litre of chlorine contains X molecules. Also, the two litres of hydrogen chloride produced would contain 2X molecules.

$$\underset{\text{(X molecules)}}{\text{Hydrogen}} + \underset{\text{(X molecules)}}{\text{Chlorine}} \longrightarrow \underset{\text{(2X molecules)}}{\text{Hydrogen chloride}}$$

Each molecule of hydrogen chloride must contain at least one atom of hydrogen; hence, 2X molecules of hydrogen chloride must contain 2X atoms of hydrogen. These 2X atoms of hydrogen are obtained from the X molecules of hydrogen contained in one litre.

X molecules of hydrogen contain 2X atoms of hydrogen

1 molecule of hydrogen contains $\frac{2X}{X} = 2$ *atoms* of hydrogen

All chemical reactions of hydrogen can be explained by assuming that the molecule of hydrogen contains two atoms; hence, experience tends to confirm the above proof.

(3) CONCLUSION. Similarly, it may be shown that each of the common gaseous elements contains two atoms per molecule. Such molecules are often referred to as *diatomic* and they are found in the following elements:

Oxygen	O_2	Chlorine	Cl_2
Hydrogen	H_2	Bromine	Br_2
Nitrogen	N_2	Iodine	I_2

5. Atomic Weights

If we accept Dalton's hypothesis that atoms exist and that those of any one element are exactly alike in weight but different from those of other elements, the next problem would naturally be the determination of the *relative weights* of these atoms. Of course, the actual weights of atoms are too small to be used and that is why we consider their relative weights. Thus, one gram of hydrogen at S.T.P. contains about 6×10^{23} hydrogen atoms.

For many years chemists used the weight of the hydrogen atom as the standard for atomic weights and they gave it a relative weight of *one.* Today, however, *the standard is the weight of an oxygen atom, which is given a relative weight of 16.* This changes the atomic weight of hydrogen to 1.0078. Thus the weight of the nitrogen atom is 14.01 as compared to the oxygen atom with a weight of 16.

An atomic weight table of the elements is found on the inside of the front cover and it will be useful in determining the molecular weights or formula weights of substances. Thus, the molecular weight of carbon dioxide can be calculated from its formula as follows:

$$CO_2 = 12 + 16 \times 2 = 12 + 32 = 44.$$

If the atomic weight of an element is expressed in grams, then it is called the gram atomic weight of the element under consideration. Thus 35.46 grams represents the gram atomic weight of chlorine.

In conclusion, *atomic weights are numbers which give us the relative weights of the atoms of the elements*, compared to the oxygen atom with a weight of 16. It is also well to remember that when elements or compounds react, they always do so in proportion to their atomic or molecular weights.

There are a number of methods for determining atomic weights but these will not be considered as they are beyond the scope of this book.

EXERCISES

1. (a) What was the purpose of Dalton's atomic hypothesis?
   (b) What are the chief postulates of Dalton's Theory?
2. Show clearly how Dalton's theory explains the laws of Conservation of Mass and Definite Proportions.
3. (a) State Avogadro's Hypothesis.
   (b) Develop the proof of the statement that the molecule of oxygen contains two atoms. Do the same for hydrogen.
4. Make a list of five diatomic molecules.
5. (a) What is the standard for atomic weights?
   (b) What is the atomic weight of an element?
6. The formula for potassium chlorate is $KClO_3$. Calculate its gram molecular weight.
7. The formula for sulphuric acid is H_2SO_4. Calculate its gram molecular weight. Do the same for cane sugar (sucrose), $C_{12}H_{22}O_{11}$.

CHAPTER XVIII

VALENCE

1. What is Valence?

HCl	H_2O	NH_3	CH_4
(hydrogen) (chloride)	(water)	(ammonia)	(methane)

An examination of the above formulas shows that the capacity of different atoms to hold hydrogen atoms in chemical combination varies; thus, one atom of chlorine holds one atom of hydrogen in chemical combination, one atom of oxygen holds two hydrogen atoms, one atom of nitrogen holds three, and one atom of carbon holds four. *Valence is the capacity of an atom or group of atoms (radical) of holding in chemical combination or displacing a definite number of hydrogen atoms.* Nitrogen, for example, has a valence of three because it holds three atoms of hydrogen in chemical combination. Zinc atoms, on the other hand, have a valence of two because the atomic weight of zinc displaces two atomic weights of hydrogen from acids. The sulphate (SO_4) radical has a valence of two because it holds two atoms of hydrogen in combination in the sulphuric acid (H_2SO_4) molecule.

2. The Standard of Valence

The atom of hydrogen has been selected as the standard and its valence is *one*. Hydrogen and all the elements which have a valence of one are said to be monovalent elements. Those with a valence of two are known as divalent elements, and those with three are trivalent. Carbon and all elements with a valence of four are called tetravalent. Phosphorus is a good example of a pentavalent (five) element and sulphur could be classed as hexavalent (six).

3. Reason for Valence

The modern chemist has shown that the atom is composed chiefly of three types of particles. These are protons, electrons, and neutrons. The proton carries a very small amount of positive electricity and it has about the same weight as a hydrogen atom. The electron is charged with negative electricity and it is extremely light, about 1/1845 of the weight of one hydrogen atom. The neutron is electrically neutral and it has the same weight as a proton. Atoms are composed of an equal number of protons and electrons and, since the amount of positive electricity carried by a proton is exactly equal to the amount on an electron, they are electrically neutral. The protons and neutrons are located in the central part of the atom, which is known as the nucleus. The electrons are outside the nucleus and they revolve around it in orbits, somewhat as the planets revolve about our sun. For this reason, these tiny particles are often called *planetary electrons* and the physical and chemical properties of an atom depend chiefly on the number and arrangement of the electrons.

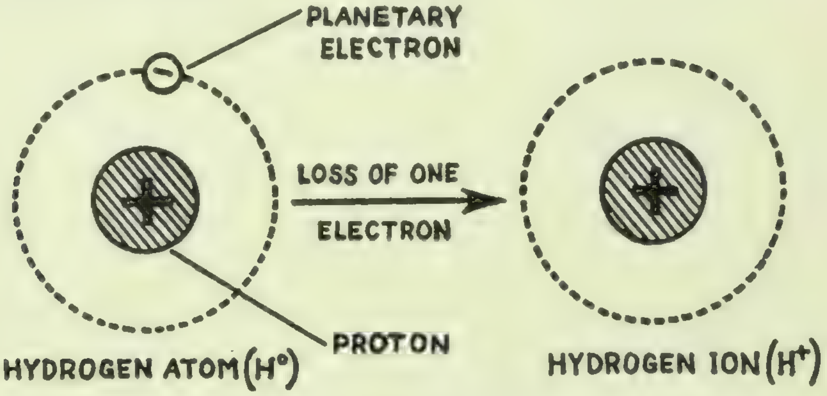


FIG. 76—HYDROGEN ION FROM HYDROGEN ATOM

Some atoms tend to give up their electrons and, when they do, the atom as a whole becomes positively charged. The resulting particle is now known as an ion. Chemists use diagrams to represent the structure of atoms and the simplest atom is that of hydrogen which is shown in Fig. 76. The plus sign (+) represents a proton and a small circle with a minus sign (−) stands for an electron. When a hydrogen atom (H°) loses one electron it becomes a hydrogen ion (H^+). The atoms of the metals tend to lose electrons to become positive ions. Thus, the sodium atom (Na°) loses one electron to form a sodium ion (Na^+); the calcium atom (Ca°) loses two electrons to form a calcium ion (Ca^{++}) and the aluminum atom (Al°) loses three electrons to produce an aluminum ion (Al^{+++}).

The atoms of non-metals, on the other hand, tend as a rule to take up electrons to give negative ions. Thus, the chlorine atom (Cl°) tends to pick up one electron to produce a chloride ion (Cl^-). The sulphur atom (S°) tends to absorb two electrons, whenever possible, to form the sulphide ion (S^{--}). The reason why some atoms tend to lose electrons and some tend to gain them will be discussed in a later chapter, when the structure of the atom will be considered in somewhat more detail.

The number of electrical charges on an ion is the same as the valence of that element. From the above discussion it is evident that there are two types of valence, positive and negative. Hydrogen and the metals have a positive valence and the nonmetals show a negative valence as a rule.

From a study of physics we know that positively charged particles will attract negatively charged particles; hence, positive ions must attract negative ions. Thus, one sodium ion would be attracted to one chloride ion to form a molecule of sodium chloride.

$$Na^+ + Cl^- \longrightarrow Na^+ \text{——} Cl^-$$

However, a calcium ion would attract two chloride ions as follows:

$$Ca^{++} + 2\ Cl^- \longrightarrow Ca \begin{array}{l} + \text{——} Cl^- \\ + \text{——} Cl^- \end{array}$$

An aluminum ion would require three chloride ions to balance its electrical charge of three positive.

$$Al^{+++} + 3\ Cl^- \longrightarrow Al \begin{array}{l} + \text{——} Cl^- \\ + \text{——} Cl^- \\ + \text{——} Cl^- \end{array}$$

From the above examples it is evident that the molecule must be electrically neutral and this fact must be remembered when writing formulas.

4. A Table of Valence

A knowledge of valence is very necessary for the proper understanding of chemistry and, in order to help the student to remember the valences of the more important elements, the following table is included.

5. Variable Valence

It has been found that certain elements show more than one valence and such elements are said to have variable valence. Thus, in the carbon monoxide (CO) molecule, carbon has a valence of two, whereas in the carbon dioxide (CO_2) molecule, carbon has a valence of four. As a matter of fact, the usual valence of carbon is four and it is rather unusual for carbon to show a valence of two. Another element which has this property of variable valence is sulphur. There are two oxides of sulphur, namely sulphur dioxide (SO_2) and sulphur trioxide (SO_3). In

TABLE 10—VALENCES OF IMPORTANT ELEMENTS AND RADICALS

Valence	Positive		Negative	
Monovalent **I**	hydrogen	H^+	fluorine	F^-
	sodium	Na^+	chlorine	Cl^-
	potassium	K^+	bromine	Br^-
	silver	Ag^+	iodine	I^-
	ammonium	NH_4^+	hydroxide	OH^-
	mercury (mercurous)	Hg^+	nitrate	NO_3^-
	copper (cuprous)	Cu^+	chlorate	ClO_3^-
			nitrite	NO_2^-
Divalent **II**	calcium	Ca^{++}	oxygen	O^{--}
	magnesium	Mg^{++}	sulphur	S^{--}
	zinc	Zn^{++}	sulphite	SO_3^{--}
	lead	Pb^{++}	sulphate	SO_4^{--}
	barium	Ba^{++}	carbonate	CO_3^{--}
	copper (cupric)	Cu^{++}		
	mercury (mercuric)	Hg^{++}		
	iron (ferrous)	Fe^{++}		
	tin (stannous)	Sn^{++}		
Trivalent **III**	aluminum	Al^{+++}	nitrogen	N^{---}
	arsenic	As^{+++}	phosphorus	P^{---}
	antimony	Sb^{+++}	phosphate	PO_4^{---}
	gold	Au^{+++}		
	bismuth	Bi^{+++}		
	iron (ferric)	Fe^{+++}		
Tetravalent **IV**	carbon	C^{++++}	carbon	C^{----}
	silicon	Si^{++++}	silicon	Si^{----}
	sulphur	S^{++++}		
	tin (stannic)	Sn^{++++}		
Pentavalent **V**	arsenic	As^{+++++}		
	antimony	Sb^{+++++}		
	nitrogen	N^{+++++}		
	phosphorus	P^{+++++}		

SO_2 sulphur has a valence of four, and in SO_3 it has a valence of six. In the case of elements, such as carbon and sulphur, a prefix indicates the number of oxygen atoms combined to one atom of the element. Thus, the prefix "di" tells us that there are two atoms of oxygen combined to one of carbon in the carbon dioxide molecule. With compounds of the metals, containing only two elements, another system has been evolved. There are two chlorides of iron, $FeCl_2$ and $FeCl_3$. $FeCl_2$ is known as ferrous chloride and $FeCl_3$ is called ferric chloride. In the ferrous compound iron has a valence of two and in the ferric compound it has a valence of three. The rule is that the compound, in which the element shows the lower valence, has the ending "ous" attached to the name of the metallic element in the compound. The other compound, in which the element shows the higher valence, has the ending "ic". A few examples are given below.

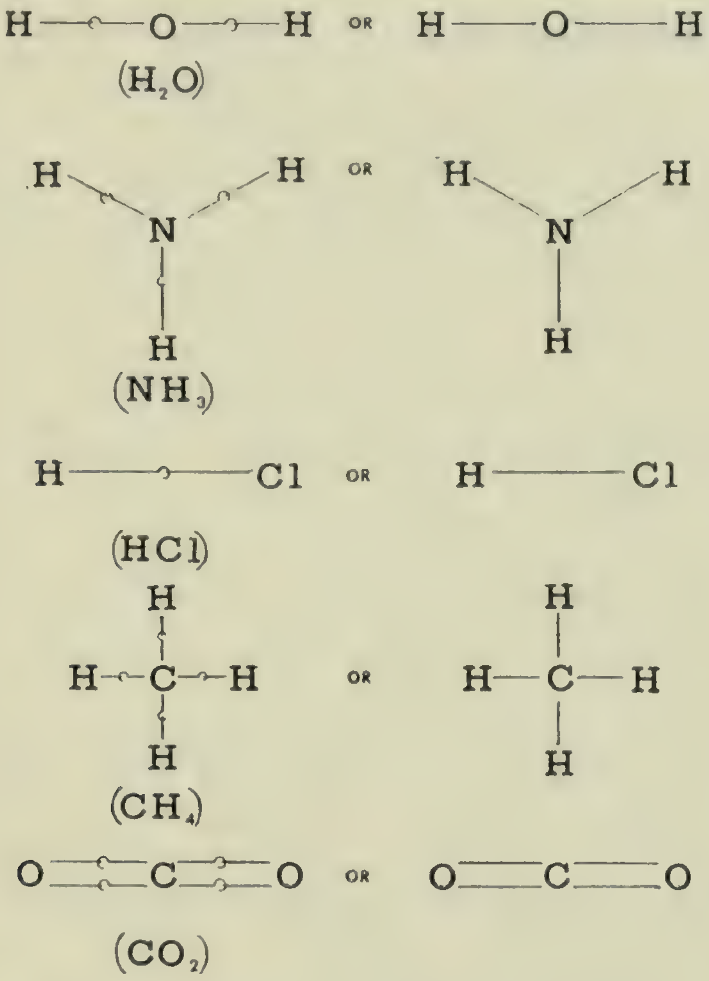


FIG. 77—DIAGRAM ILLUSTRATING VALENCE

HgCl	Mercur*ous* Chloride
$HgCl_2$	Mercur*ic* Chloride

$SnCl_2$	Stann*ous* Chloride
$SnCl_4$	Stann*ic* Chloride

$CuCl$	Cupr*ous* Chloride
$CuCl_2$	Cupr*ic* Chloride

6. Structural Formulas

The ordinary formulas used in writing equations are known as molecular formulas but they do not show how the atoms are arranged in space. To indicate the arrangement of the atoms in the molecule, the chemist has devised a type of formula which is known as a structural formula. A few examples are shown in Fig. 77.

EXERCISES

1. (a) What is valence?
   (b) What is the standard for valence?
2. Discuss carefully the reason for valence.
3. What is meant by variable valence? Illustrate by means of the chlorides of tin and copper.
4. What is a structural formula? Write the structural formulas for methane and carbon tetrachloride.
5. Write formulas for the following compounds: sodium sulphate, silver phosphate, calcium iodide, aluminum bromide, stannic chloride, calcium phosphate, cuprous nitrate, cupric bromide, potassium sulphide, ammonium sulphate, zinc phosphate, stannous iodide, mercurous sulphite, cupric carbonate, bismuth nitrite, ferric bromide, ammonium nitrite, silver nitrate.

CHAPTER XIX

SYMBOLS, FORMULAS AND EQUATIONS

1. Symbols

Symbols were introduced in Chapter 9, when it was found that a *symbol is a letter or a pair of letters which represents a chemical element.* However, a symbol is more than a contraction of the name of an element. It represents one atom of an element and it also stands for the atomic weight of the element in question. For example, O is the symbol for the element oxygen and it stands for one atom of oxygen. In addition, the symbol O represents one atomic weight of the element, being 16 in this case.

In summary it can be said that a symbol represents:

(1) The name of a chemical element.
(2) One atom of an element.
(3) One atomic weight of an element.

2. Formulas

A formula may be defined as a combination of symbols to represent one molecule of an element or a compound. For example, NaCl represents one molecule of the compound sodium chloride which is composed of one atom of the element sodium (Na) combined with one atom of the element chlorine (Cl). H_2O represents a molecule of the compound water and the formula shows that two atoms of hydrogen are combined with one atom of oxygen to form one molecule of this substance. It should be remembered that a number placed before a formula tells us how many molecules are being considered. Thus, $5H_2O$ represents five molecules of water and $10Cl_2$ means ten molecules of the element chlorine.

The formula of a substance means a great deal to a chemist, much more than it does to the layman. Nearly everyone knows that H_2O stands for water but only a student of chemistry realizes that it represents one molecule of the chemical compound water. Furthermore, the formula H_2O tells us that every molecule of water is composed of two atoms of hydrogen combined with one atom of oxygen. It also indicates that 2.016 parts by weight of hydrogen combine with exactly 16 parts by weight of oxygen. The formula of a substance also represents the molecular weight or formula weight. In the case of water this value is 18.016. If the material under consideration is a gas, or can be changed into a gas without decomposition, the formula represents 22.4 litres at S.T.P. It will be remembered that 22.4 litres is known as the gram molecular volume (G.M.V.) because the molecular weight of a substance expressed in grams always occupies 22.4 litres at S.T.P. In the case of simple compounds, containing only two elements, the formula can give us the valence of one of the elements in the molecule. Of course, the valence of one element must be known. If we know that hydrogen has a valence of one, then the formula H_2O tells us that oxygen has a valence of two since one atom of oxygen holds two atoms of hydrogen in chemical combination.

From the above discussion it is apparent that a formula represents a number of important chemical facts which are summarized below.

A formula represents the following facts:

(1) One molecule of a substance.

(2) What atoms and how many are present in the molecule.

(3) Proportions by weight in which the atoms are combined in the molecule.

(4) The molecular weight of the substance.

(5) The volume of 22.4 litres, if a gas, or if it can be changed into a gas without decomposition.

(6) Valence, if dealing with a binary compound (two elements only).

3. Determination of the Formula of a Compound

The results of chemical analyses of a compound are usually expressed in percentages and from this information the molecular or correct formula may be derived, if the molecular weight is known or can be calculated. As an example, let us consider the determination of the correct formula for water. There are four distinct steps in this process and this fact should be remembered by students when attempting to solve problems of this type.

(1) DETERMINE BY EXPERIMENT WHAT ELEMENTS ARE PRESENT IN THE COMPOUND UNDER CONSIDERATION. In other words the material is subjected to qualitative analysis. In the case of water we find that two elements are present in it. These are hydrogen and oxygen.

(2) DETERMINE THE PROPORTIONS IN WHICH THE CONSTITUENTS OF THE COMPOUND ARE PRESENT. That is, a quantitative analysis of the substance is carried out and for water the following results are obtained:

Hydrogen = 11.19% by weight
Oxygen = 88.81% by weight.

(3) DETERMINE THE RELATIVE NUMBER OF ATOMS OF THE VARIOUS ELEMENTS IN THE COMPOUND. This relationship is sometimes called the atomic ratio. To secure this information we must use our knowledge of the atomic weights of these elements, hydrogen 1.008 and oxygen 16. The analysis shows that 11.19 grams of hydrogen is combined with 88.81 grams of oxygen in every 100 grams of water. If we divide each of these weights by the corresponding atomic weights, we shall obtain values that will give us the relative number of hydrogen and oxygen *atoms* in water molecules.

$$\frac{11.19}{1.008} = 11.10 = \text{number of atomic weights of hydrogen in 100 grams of water.}$$

$$\frac{88.81}{16} = 5.55 = \text{number of atomic weights of oxygen in 100 grams of water.}$$

This result shows that for every 11.10 hydrogen atoms there are 5.55 oxygen atoms. According to Dalton's atomic theory, fractions of atoms cannot exist; so, we must change this ratio to the simplest one of whole numbers:

$$\frac{11.10}{5.55} = \frac{2}{1}$$

From the above it is evident that there are two hydrogen atoms for every one oxygen atom in water; hence, the *simplest formula* for a water molecule is H_2O.

(4) DETERMINE THE CORRECT MOLECULAR FORMULA. The simplest formula is sometimes the correct one but such is not

always the case. H_4O_2, H_6O_3, would be satisfactory formulas for water as far as the information considered above indicate As. knowledge of the molecular weight of water will enable us to select the correct formula for its molecule because H_2O represents a molecular weight of 18, H_4O_2 one of 36, and H_6O_3 one of 54. Experiment shows that the molecular weight of water, at least in the gaseous state, is 18; so, H_2O is not only the simplest formula, but it is also the correct one for water in the gaseous state.

In the case of many substances, especially solids, the molecular weight cannot be determined and in such cases the simplest formula is used as the correct one.

Example 1

A gas is composed of 92.3% carbon and 7.7% hydrogen. The molecular weight of the gas is 78. Calculate the correct molecular formula of the compound.

Atomic ratio—

$$\text{Carbon} = \frac{92.3}{12} = 7.7 \text{ atoms of carbon}$$

$$\text{Hydrogen} = \frac{7.7}{1} = 7.7 \text{ atoms of hydrogen.}$$

The simplest formula of this compound is CH and its formula weight is 1 + 12, or 13.

$$\frac{\text{Correct molecular weight}}{\text{Formula weight of simplest formula}} = \frac{78}{13} = 6$$

Thus, the correct molecular formula of the compound must contain six atoms of carbon and six atoms of hydrogen and the correct molecular formula is C_6H_6.

Example 2.

The percentage composition of a solid is as follows:

Sodium = 32.37
Sulphur = 22.58
Oxygen = 45.05

Calculate the simplest formula of this substance.

Atomic ratio—

$$\text{Sodium} = \frac{32.37}{23} = 1.41$$

$$\text{Sulphur} = \frac{22.58}{32} = 0.705$$

$$\text{Oxygen} = \frac{45.05}{16} = 2.81$$

or, Na : S : O = 1.41 : 0.705 : 2.81

That is, these atoms are combined in the ratio of 2 to 1 to 4. From the above it is evident that the simplest formula for this solid is Na_2SO_4, which is the formula for sodium sulphate.

Another Method. If the molecular weight of the substance is given, a simpler method can be used. However, it must be remembered that this method can be used only if the molecular weight of the substance under consideration is known or it can be calculated from the information given in the problem. This is illustrated by the following example.

The molecular weight of acetylene is 26.02 grams. Its percentage composition is found to be carbon 92.31, hydrogen 7.69. What is its correct formula?

Since 92.31% of the substance is carbon, one gram molecular weight (G.M.W.) contains $\frac{92.31}{100} \times 26.02 = 24.02$ grams of carbon. But one gram atomic weight of carbon = 12.00 grams. Therefore, one molecular weight of acetylene contains $\frac{24.02}{12.00}$, or 2 atomic weights of carbon. Thus, each molecule of acetylene contains two carbon atoms.

Similarly, since 7.69% of acetylene is hydrogen, one gram molecular weight contains $\frac{7.69}{100} \times 26.02 = 2.004$ grams of hydrogen. But one gram atomic weight of hydrogen = 1.008 grams. Therefore, one molecular weight of acetylene contains $\frac{2.004}{1.008}$, or two atomic weights of hydrogen. Thus, each molecule contains two hydrogen atoms. The molecular formula of acetylene is, therefore, C_2H_2.

4. Equations

When powdered iron is heated in the laboratory with sulphur, a chemical reaction takes place which produces a new substance, namely iron sulphide. Chemists represent this chemical change by means of the following combination of symbols, which is called an equation.

$$\underset{\text{Iron}}{Fe} + \underset{\text{Sulphur}}{S} \longrightarrow \underset{\text{Iron sulphide}}{FeS}$$

The equation for the decomposition of potassium chlorate is as follows:

$$\underset{\substack{\text{potassium}\\\text{chlorate}}}{2\ KClO_3} \longrightarrow \underset{\substack{\text{potassium}\\\text{chloride}}}{2\ KCl} + \underset{\text{oxygen}}{3O_2\uparrow}$$

Another well known reaction, the burning of magnesium ribbon in air, can be represented by the following equation:

$$\underset{\text{magnesium}}{2\ Mg} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\text{magnesium oxide}}{2\ MgO}$$

From the above examples of chemical equations it is observed that *an equation consists of a combination of symbols and formulas and it represents a real chemical reaction.*

To write an equation we must know the following facts:

(1) That a chemical change occurs.

(2) What substances react and what materials are formed.

(3) Formulas of starting substances and of the products.

5. Types of Chemical Reactions

Chemical reactions have been classified into four types and these, along with examples of each, are given below.

1. COMBINATION, OR SYNTHESIS. In this type of reaction, two or more substances, elements or compounds, *combine* to form a more complex substance.

$$2\ H_2 + O_2 \longrightarrow 2\ H_2O$$

$$Fe + S \longrightarrow FeS$$

$$S + O_2 \longrightarrow SO_2$$

$$3\ Fe + 2\ O_2 \longrightarrow Fe_3O_4$$

$$2\ Na + Cl_2 \longrightarrow 2\ NaCl$$

$$H_2O + SO_2 \longrightarrow H_2SO_3$$

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

2. SIMPLE DECOMPOSITION, OR ANALYSIS. This reaction is the reverse of the first type and it involves the breakdown of only one substance into two or more simpler substances.

$$2\ HgO \longrightarrow 2\ Hg + O_2\uparrow$$
$$2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2\uparrow$$
$$2\ H_2O \longrightarrow 2\ H_2\uparrow + O_2\uparrow$$
$$CaCO_3 \longrightarrow CaO + CO_2\uparrow$$

3. SIMPLE DISPLACEMENT. In this type of reaction one element takes the place of some other element or elements in a compound. It is also known as *simple replacement* or *substitution*.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$$
$$2\ Na + 2\ H_2O \longrightarrow 2\ NaOH + H_2\uparrow$$
$$CuO + H_2 \longrightarrow Cu + H_2O$$
$$Fe + CuSO_4 \longrightarrow FeSO_4 + Cu$$
$$3\ Fe + 4\ H_2O \longrightarrow Fe_3O_4 + 4\ H_2\uparrow$$

4. DOUBLE DECOMPOSITION. In this type, two compounds exchange metallic atoms or a metal is exchanged for hydrogen. It is also known as *double replacement* or *metathesis*.

$$BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4\downarrow + 2\ NaCl$$
$$AgNO_3 + HCl \longrightarrow AgCl\downarrow + HNO_3$$
$$NaOH + HCl \longrightarrow NaCl + H_2O$$

EXERCISES

Section A

1. (a) What does a symbol represent?
   (b) Is H a symbol or a formula? What about 2N, Cl_2, 5 O, Fe?
2. Give the meaning of each symbol and figure in the following expressions: Na, S, 6 H_2O, HNO_3, $CuSO_4.5H_2O$.
3. (a) What is the symbol for oxygen?
   What is its formula?
   (b) What is the difference between the atom and the molecule of oxygen?
4. Define the chemical terms: *symbol, formula, equation.*
5. (a) What does a formula represent?
   (b) State all that the formula NH_3 (a gas) is meant to indicate.
6. What facts must be known before a chemical equation can be written?
7. What important facts about a chemical reaction are not expressed in a chemical equation?

8. Write the equations for the following chemical reactions, and state the type of chemical reaction involved:
   (a) A solution of barium chloride reacts with a solution of sodium sulphate.
   (b) Mercuric oxide is heated.
   (c) Copper oxide is heated while hydrogen gas is passing over it.
   (d) Sulphur is burned in oxygen.

9. Balance the following equations and state the type of reaction involved.

   (a) 2 $HgO \longrightarrow Hg + O_2\uparrow$
   (b) $KClO_3 \longrightarrow KCl + O_2\uparrow$
   (c) $H_2O \longrightarrow H_2\uparrow + O_2\uparrow$
   (d) $Mg + O_2 \longrightarrow MgO$
   (e) $Fe + O_2 \longrightarrow Fe_3O_4$
   (f) $Cu + O_2 \longrightarrow CuO$
   (g) $Na + H_2O \longrightarrow NaOH + H_2\uparrow$
   (h) $Zn + HCl \longrightarrow ZnCl_2 + H_2\uparrow$
   (i) $Fe + H_2O \longrightarrow Fe_3O_4 + H_2\uparrow$

Section B

1. A gaseous compound has the following composition: 96.2% As, 3.8% H. A volume of 1 litre of this gas measured at 0° C. and 760 mm. of mercury weighs 3.48 g. Find the molecular formula of the compound.

2. The molecular weight of cyanogen is 52.02. Its percentage composition is found to be carbon 46.08, nitrogen 53.92. What is its correct formula?

3. A substance on analysis yields 43.75% nitrogen, 6.25% hydrogen and 50.0% oxygen. Its molecular weight is 64. Find the formula for this substance.

4. The percentage composition of a substance is found to be 80% carbon and 20% hydrogen. Its vapour at S.T.P. is 15 times as heavy as hydrogen. What is the molecular formula for the substance.

5. A gas yielded on analysis 85.72% carbon and 14.28% hydrogen. The density of the gas at S.T.P. is 1.25 grams per litre. Find the molecular formula of the gas.

6. An oxide of aluminum has the following composition: aluminum 52.89% and oxygen 47.09%. Determine the simplest formula of this oxide.

7. A sample of a chloride of iron weighing 8.1105 g. was found to contain 2.7920 g. of iron. Calculate its formula.

8. The composition of a copper ore is as follows: copper 79.45%, sulphur 20.32%. What is the simplest formula?

9. If 26 grams of an oxide of mercury are required to give, by heating, one gram of oxygen, what is the simplest formula of the oxide?
10. A substance on analysis gave the following percentage composition: carbon 10.05%, hydrogen 0.84%, chlorine 89.10%. Derive the simplest formula of the substance.

CHAPTER XX

CHEMICAL CALCULATIONS

The chemical equation is of the utmost importance to the chemical engineer. By means of it he calculates the quantity of various substances required for a given reaction and how large an amount of product he may hope to obtain. In actual practice, however, he seldom secures the theoretical yield of the product as calculated from the equation. These important calculations of industrial chemists are all based on the chemical equations of the reactions involved and they can be classified into several types.

1. Molecular Weight of a Compound from the Formula

In the previous chapter it was found that a formula represents the molecular weight of the material under consideration. To calculate the molecular weight of a substance from its formula, it is necessary simply to add the weights of all the atoms in the molecule. The molecular weight is also known as *formula weight.*

EXAMPLE 1.

The formula for calcium carbonate is $CaCO_3$. Find its molecular weight. ($Ca = 40$; $C = 12$; $O = 16$)

$$CaCO_3 = 40 + 12 + (3 \times 16) = 100$$

EXAMPLE 2.

The formula for sulphuric acid is H_2SO_4. Find its formula weight. ($H = 1$; $S = 32$; $O = 16$)

$$H_2SO_4 = (2 \times 1) + 32 + (4 \times 16) = 98$$

2. Percentage Composition of a Compound from its Formula

If the formula of a compound is known, and if an atomic weight table is available, the percentage of each element present in the compound can be calculated.

EXAMPLE 1.

The formula of carbon tetrachloride is CCl_4. Calculate its percentage composition. (Atomic weight: C, 12; Cl, 35.5)

The molecular weight of $CCl_4 = 12 + (4 \times 35.5) = 154$

$$\% \text{ carbon} = \frac{12}{154} \times 100 = 7.79$$

$$\% \text{ chlorine} = \frac{142}{154} \times 100 = \frac{92.21}{100.00}$$

EXAMPLE 2.

The formula of calcium carbonate is $CaCO_3$. Calculate its percentage composition. (Atomic weights: Ca, 40; C, 12; O, 16)

The molecular weight of $CaCO_3 = 40 + 12 + (3 \times 16) = 100$

$$\% \text{ calcium} = \frac{40}{100} \times 100 = 40$$

$$\% \text{ carbon} = \frac{12}{100} \times 100 = 12$$

$$\% \text{ oxygen} = \frac{48}{100} \times 100 = \frac{48}{100}$$

In this type of problem the sum of the percentages obtained should, of course, be 100. If such is not the case there is a mistake in your method or in your arithmetic.

3. Quantitative Meaning of Equations

In the last chapter it was found that a properly balanced equation furnishes much valuable information. It tells what substances react and what the products are. It also gives the number of molecules of each substance involved. Furthermore, since the molecular weight of any substance can be readily calculated from its formula and the atomic weights, we have *a method of calculating the relative weights of the different substances in the equation.*

For example, in the equation for the laboratory preparation of oxygen by heating potassium chlorate, the relative weights of potassium chlorate, potassium chloride, and oxygen can be calculated as follows:

$$\begin{array}{ccc} 2\,KClO_3 & \longrightarrow 2\,KCl & + \; 3\,O_2 \\ (2 \times 122.5) & (2 \times 74.5) & (3 \times 32) \\ 245 \text{ g.} & 149 \text{ g.} & 96 \text{ g.} \end{array}$$

The gram molecular weight (G.M.W.) of each substance may be found by adding the atomic weights of the elements involved:

G.M.W. of $KClO_3$ = $39 + 35.5 + (16 \times 3) = 122.5$ g.
G.M.W. of KCl = $39 + 35.5 = 74.5$ g.
G.M.W. of O_2 = $2 \times 16 = 32$ g.

Since there are two molecules of potassium chlorate and of potassium chloride in the equation, we multiply their gram molecular weights by two. In the case of oxygen, there are three molecules and hence we multiply its molecular weight by three.

From the above it is evident that 245 g. of potassium chlorate will produce 149 g. of potassium chloride and 96 g. of oxygen. However, it must be remembered that *245 parts by weight of potassium chlorate give 149 parts by weight of potassium chloride and 96 parts by weight of oxygen*, regardless of what units of weight are used. For example, 245 lb. of the chlorate decomposes into 149 lb. of the chloride and 96 lb. of oxygen.

4. Problems Involving Weights Only

The information given above makes it possible to solve problems such as the following:

EXAMPLE 1.

How many grams of potassium chlorate are needed to prepare 20 grams of oxygen?

(1) Write the balanced equation:

$$2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2$$

(2) Write under the formulas the gram molecular weights, taken the proper number of times.

$$\begin{array}{ccc} 2\ KClO_3 & \longrightarrow 2\ KCl + & 3\ O_2 \\ (2 \times 122.5) & & (3 \times 32) \\ 245\text{ g.} & & 96\text{ g.} \end{array}$$

(3) Write out the steps in solving the simple problem in arithmetic.

$$96\text{ g. of } O_2 \text{ require } 245 \text{ g. of } KClO_3$$

$$1\text{ g. of } O_2 \text{ requires } \frac{245}{96} \text{ g. of } KClO_3$$

$$20\text{ g. of } O_2 \text{ require } \frac{245}{96} \times 20 = 51 \text{ g.}$$

The answer is 51 grams of $KClO_3$.

EXAMPLE 2.

What weight of lead will be required to combine with 10 grams of sulphur to form lead sulphide (PbS)?

(1) $Pb + S \longrightarrow PbS.$

(2) 207.21 g. 32.06 g.

(3) 32.06 g. of S need 207.21 g. of Pb

$$1 \text{ g. of S needs } \frac{207.21}{32.06} \text{ g. of Pb}$$

$$10 \text{ g. of S need } \frac{207.2}{32.06} \times 10 = 64.63 \text{ g.}$$

The answer is 64.63 grams of lead.

5. Problems Involving Gas Volumes Only

If both the substance given and that required are gases, and volume relations alone are involved, the problem becomes a very simple one. According to Avogadro's hypothesis, equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules. It is evident, then, that the numbers of molecules in the equation for any reaction of this kind are in the same ratio as the volumes of gases involved; so the volumes of the gases may be obtained directly from the balanced equation. The equation for the synthesis of ammonia:

$$N_2 + 3\ H_2 \longrightarrow 2\ NH_3$$

tells us that *one* volume of nitrogen reacts with *three* volumes of hydrogen to produce two volumes of ammonia, because these are the number of molecules of each substance in the equation. The same proportions would hold no matter what unit of volume is used.

EXAMPLE.

How many cubic feet of carbon dioxide is formed from the combustion of 10 cu. ft. of carbon monoxide, if both gas volumes are measured under the same conditions? The equation for the reaction is:

$$2\ CO + O_2 \longrightarrow 2\ CO_2$$
$$2 \text{ vols.} + 1 \text{ vol.} \longrightarrow 2 \text{ vols.}$$
$$2 \text{ cu. ft. of } CO \longrightarrow 2 \text{ cu. ft. of } CO_2$$
$$1 \text{ cu. ft. of } CO \longrightarrow 1 \text{ cu. ft. of } CO_2$$
$$10 \text{ cu. ft. of } CO \longrightarrow 10 \text{ cu. ft. of } CO_2$$

The answer is 10 cu. ft. of CO_2.

6. Problems Involving Weights and Gas Volumes

The important fact to remember in problems of this kind is that *one gram molecular weight of any gas at S.T.P. always occupies 22.4 litres.*

EXAMPLE 1.

What volume of oxygen at S.T.P. will be formed by decomposing 49 g. of potassium chlorate?

(1) Write the balanced equation

$$2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2$$

(2) Write under the formulas the proper weights and volumes

$$\begin{array}{ccc} 2\ KClO_3 \longrightarrow 2\ KCl + & & 3\ O_2 \\ (2 \times 122.5) & & (3 \times 22.4) \\ 245\text{ g.} & & 67.2\text{ litres} \end{array}$$

(3) Write out the steps in solving the problem in arithmetic

245 g. of $KClO_3$ produce 67.2 litres of O_2 at S.T.P.

1 g. of $KClO_3$ produces $\frac{67.2}{245}$ litres of O_2 at S.T.P.

49 g. of $KClO_3$ produce $\frac{67.2}{245} \times 49 = 13.44$ litres.

The answer is 13.44 litres of O_2 at S.T.P.

EXAMPLE 2.

How many litres of oxygen at 20° C. and a pressure of 750 mm. will be formed by the electrolysis of 9 g. of water? This is a combination of a gas law problem with the type which we have been considering.

(1) Write the balanced equation

$$2\ H_2O \longrightarrow 2\ H_2 + O_2$$

(2) Write under the formulas the proper weights and volumes

$$\begin{array}{ccc} 2\ H_2O \longrightarrow 2\ H_2 + & & O_2 \\ (2 \times 18) & & \\ 36\text{ g.} & & 22.4\text{ litres at S.T.P.} \end{array}$$

(3) Statements of solution

36 g. of water produce 22.4 litres of O_2 at S.T.P.

1 g. of water produces $\frac{22.4}{36}$ litres of O_2 at S.T.P.

9 g. of water produce $\frac{22.4}{36} \times 9 = 5.6$ litres of O_2 at S.T.P.

(4) Application of the gas laws.

$$5.6 \times \frac{293}{273} \times \frac{760}{750} = 6.0 \text{ litres.}$$

The answer is 6.0 litres of O_2 at 20° C. and 750 mm.

EXERCISES

In solving these problems, use values for the atomic weights to the nearest whole number, but in the case of chlorine use 35.5.

1. What is the percentage of each element in the following compounds: HCl, $BaCl_2$, Na_2SO_4, H_2SO_4, C_2H_5OH?
2. How much potassium chlorate must be used to generate 10 grams of oxygen?
3. What volume of nitrogen is needed to combine with 18 litres of hydrogen? What volume of ammonia is formed?
4. What volume of oxygen, measured at 20° C. and 750 mm. may be made by the complete decomposition of 20 g. of $KClO_3$?
5. What weight of water must be decomposed by electrolysis to secure 20 litres of hydrogen at 27° C. and 800 mm.?
6. Calculate the volume of hydrogen measured at 20° C. and 770 mm. of mercury that would be obtained if 10 g. zinc were allowed to react completely with excess dilute sulphuric acid.
7. Calculate the volume of oxygen measured at 300° C. and 740 mm. that would react completely with 1 g. carbon to form carbon dioxide. What volume of carbon dioxide measured under the same conditions of temperature and pressure would be obtained?
8. Calculate the percentage of water of crystallization in the following compounds: $Na_2CO_3.10H_2O$, $CuSO_4.5H_2O$, $MgSO_4.7H_2O$, $BaCl_2.2H_2O$.
9. What weight of calcium must be used to react with an excess of water to obtain 10 litres of hydrogen at 127° C. and 800 mm.?
10. What weight of sodium must be used to react with an excess of water to obtain 5 litres of hydrogen at −23° C. and 600 mm.?
11. What weight of oxygen must be used to react completely with 6 g. carbon to produce carbon dioxide? What would be the volume of carbon dioxide formed at 27° C. and 720 mm.?

CHAPTER XXI

CARBON

1. Importance of Carbon in Nature and Industry

In many respects, carbon is the most interesting of all the chemical elements; it is also one of the most useful. It makes up less than .03 per cent of the earth's surface and yet this comparatively small quantity of the element is of the greatest importance. This is shown by the fact that over 300,000 compounds of the element are found in nature or have been prepared by chemists. It is interesting to know that this is about twelve times the total number of compounds of all the other chemical elements. Furthermore, the bodies of plants and animals are made up chiefly of carbon compounds. Carbon or carbon compounds supply man with nearly all of his food, fuel and clothing. The combustion of carbon or carbon compounds produces much of the energy required in our industries, and this element or its compounds assist in the production of such important materials as steel, glass, bricks, lime, cement, explosives, fertilizers, plastics, insecticides, dyes, medicines, solvents and many other commodities which are so essential to our modern civilization. There is no doubt that carbon ranks with oxygen, hydrogen and nitrogen as one of the four elements most important to mankind.

2. Occurrence

Carbon, in the free state or uncombined, is found in nature in several forms. The *diamond* is the purest form of natural carbon. *Graphite*, or plumbago, which is next to the diamond in purity, is found in limited quantities in nature, and it is a valuable mineral. *Coal*, which is an impure form of carbon, is found in a great many regions of the world.

In the combined state, carbon is found quite widespread in nature. Enormous quantities of carbon, far exceeding that in coal, occur in combination in such rocks as the limestones and the dolomites. These minerals often make up huge mountain ranges. Petroleum and natural gas are mixtures of carbon compounds and these materials are very important in modern times. The bodies of plants and animals are made up of a large percentage of carbon compounds. It has been estimated that the body of a man, weighing 150 lbs., contains about 25 lbs. of the element carbon in chemical combination.

3. The Crystalline Forms of Carbon

Carbon is an *allotropic* element; that is, it exists in two or more different forms in the same state.

TABLE 11—FORMS OF CARBON

Crystalline	Amorphous (Non-crystalline)
Diamond Graphite	Coal Coke Charcoal Animal Charcoal (bone-black) Lampblack (carbon black)

Each of the varieties of carbon listed in the above table will now be considered in some detail, starting with the crystalline forms.

(1) THE DIAMOND. (a) *Occurrence.* As already mentioned, this is the purest form of carbon found in nature. Diamonds are found chiefly in South Africa, Brazil and India. As they occur in nature, diamonds are usually covered with a rough coating and they have the appearance of ordinary rough stones, hardly transparent, and with little appearance of being crystals. To make them into gems, they are ground, or "cut," in such a way that they will reflect light from a number of different faces; in other words, they sparkle in the light.

In the South African mines, which supply a quarter of the world's output, the diamond-bearing "blue earth" is washed across table-like surfaces covered with grease, to which the diamonds stick while the dirt washes away. Then the diamonds are graded, by sorting through a succession of screens with holes of different sizes, before being shipped to Europe for their cutting. The large and flawless gems are used as jewels and the small or imperfect ones find many uses in industry.

The weight of the diamond is expressed in carats. A carat is equal to about 0.2 grams.

The largest diamond known was found in South Africa in 1905 and weighed 3032 carats (1.37 pounds) before being cut. This was called the Cullinan diamond and it was presented to

King Edward VII by the South African government. It was cut into several stones, two of which weighed 516 and 309 carats each, and the largest of these is now set in the head of the king's sceptre.

(b) *Properties of the Diamond.* The density of the diamond is 3.5, and though brittle, it is the *hardest* of all natural substances. It can be scratched or polished only by rubbing with diamond powder. A diamond of suitable shape will curl shavings off plate glass as readily as a carpenter's plane will remove shavings from a board. The diamond has a *high refractive index* and its property of scattering light to such an extent makes it valuable as a gem. Pure diamonds are perfectly *transparent* and generally *colourless,* but many are coloured due to traces of impurities. Sometimes the coloured ones, if perfect, are more valuable than the colourless varieties. For example, the famous (blue) Hope diamond, weighing only 44.5 carats, sold for a much higher price than a colourless gem of the same weight. In addition to blue diamonds, red, yellow, brownish-black, and green are known.

Lavoisier was the first to show that carbon dioxide is formed by the combustion of the diamond in pure oxygen. A few years later, in 1814, Sir Humphrey Davy showed that carbon dioxide is the only product formed when diamonds burn in oxygen. He determined the relationship between the weight of the diamond burned and the carbon dioxide produced and, in this way, he proved that the diamond is pure carbon. It has been found that diamonds burn in pure oxygen at about 700° C., and in the air at about 900° C. They are not attacked by most chemicals, but they will dissolve in molten iron.

(c) *Uses of the Diamond.* The diamond has great value because people like to use it as a gem. The discovery of very large diamond deposits in new regions in South Africa would have lowered the commercial value of the stones if the government had not gained control of these fields and carefully regulated the production.

Most of the *black diamonds,* also known as *carbonado* or *bort,* come from Brazil. They are valueless as gems, but they have many important uses in the industrial world. Nearly every industry uses diamonds in one or more of its processes.

Diamonds are used for *cutting* the hardest of metals with great accuracy. They are also used for *sharpening* modern machining and grinding tools, which have been responsible, to a large extent, for bringing about modern large scale production with its greater speed and lower costs.

Industrial diamonds play their part in producing electric light filaments, cutting and shaping stone, marble, and granite in a fraction of the time previously required for such operations.

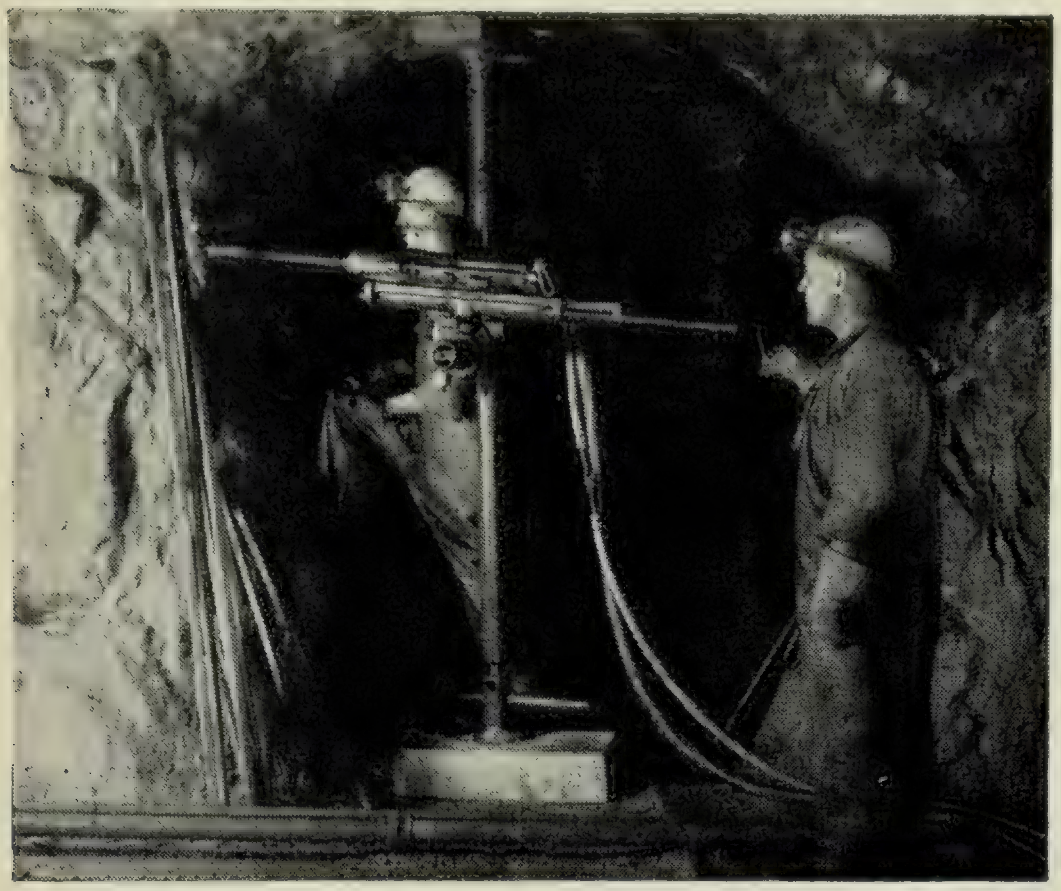


Fig. 78—The Diamond Drill is a Very Important Tool in Mining Operations. There is No Rock Through Which the Diamond Cannot Cut.

The diamond drill is a very important tool of the mining engineer, because there is no rock through which the diamond cannot cut; the hardness of the bit enables borers to cut through 18 inches of the hardest granite in an hour. It is interesting to know that the crown of diamonds for cutting the two-inch hole in mining operations costs about $5,000.

Diamonds are also used in the cutting of glass and, in the form of dust, it is a valuable polishing powder.

(d) *Artificial Production of Diamonds.* Many attempts have been made to produce diamonds artificially. In 1893, Moissan, a French chemist, was successful in producing a few real diamonds, but they were too small (the largest being about 0.5 mm. in diameter) to have any commercial value. He dissolved sugar charcoal in melted iron and cooled the molten metal suddenly by plunging it into water. Under these conditions the carbon crystallized in the iron in the form of diamonds. The iron was then dissolved in hydrochloric acid, leaving the diamonds as an insoluble residue. By similar methods, other chemists have produced somewhat larger diamonds, but this is not a practical method of producing diamonds commercially.

(2) Graphite. (a) *Occurrence.* This form of carbon is found in nature in large quantities in many places, especially in Ceylon, Siberia, the United States, Mexico, and Canada.

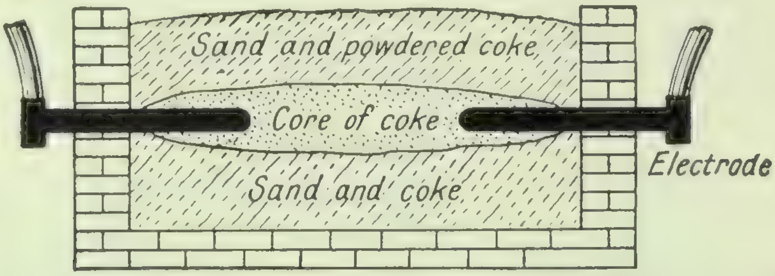


Fig. 79—Electric Furnace Used in the Manufacture of Graphite

(b) *The Commercial Production of Graphite.* Much commercial graphite is manufactured in the electric furnace from anthracite coal or coke. The process was invented by the American chemist Acheson and it is carried out on a large scale at Niagara Falls. When any form of carbon is heated, out of contact with air, in the electric furnace to a temperature of at least 3500° C., the vapour produced condenses to graphite. The Acheson process for making graphite is based on this fact. In this method anthracite coal or coke is placed between the electrodes of the furnace, which are joined by a core of coke. The charge is covered with a layer of sand and coke to keep out the oxygen of the air. A powerful alternating electric current passes through the charge and, because coke is a poor conductor of electricity, its resistance to the current produces large quantities of heat, which raise the mixture to the desired temperature. Under the influence of the intense heat the amorphous carbon of the coke is changed into graphite. When graphite is prepared in this way, it is more uniform in composition and free from grit, and, as a rule, the artificially prepared product is better than the natural material.

(c) *Properties of Graphite.* Graphite is a glistening, greyish-black solid. It is soft and greasy to the touch. Graphite is a crystalline substance and it leaves a mark when drawn across paper. The name graphite, from the Greek word which means "to write," was given to the substance due to this property. Graphite is a good conductor of heat and electricity, conducting the current better than any other form of carbon. Like the diamond it is chemically inert, and it is not attacked by most chemical reagents. It burns in oxygen at a temperature of about 700° C. to produce carbon dioxide. Since it was once thought to be some compound of lead, graphite is sometimes known as *plumbago* or *black lead*.

(d) *Uses of Graphite.* Graphite is used for the core of so-called "lead" pencils. The "lead" of a pencil is made up of a mixture of graphite, clay, and wax. The "hardness" of the lead depends upon the proportions in which the components are mixed. Soft "leads" contain more graphite and less clay than hard "leads."

Because of its chemical inactivity, graphite is used to make crucibles in which metals are melted in the production of alloys and high-grade steel. Since graphite is not affected by electricity, it is used to make electrical conductors and electrodes. It is also an excellent lubricant because its small crystals tend to slide over one another under pressure. Graphite is also used in making stove polishes and as a pigment in paints for protecting iron. A coating of graphite makes non-conducting substances good conductors of the electric current, and so it is placed upon wax moulds which are to be covered with metal by the process of electrolysis in the electrotyping method of printing.

4. The Amorphous Forms of Carbon

Many forms of carbon are said to be amorphous, although research chemists, using X-ray analysis, have shown that these so-called amorphous forms of carbon are really composed of crystals which are the same as those of graphite; they have an amorphous appearance because of the very small size of the crystals. These forms, such as charcoal, usually have more porous structures than graphite, or they form soft and very bulky powders. The most important forms of "amorphous" carbon are found in coal, coke, wood charcoal, animal charcoal or bone-black, and lampblack. These will now be considered in detail in the above order. It should be noted, however, that none of them is pure carbon, and some of them contain high percentages of impurities.

(1) COAL. (a) *Industrial Importance.* The industry of the world depends chiefly upon coal for its supply of energy. This energy is made available by combustion of the coal beneath boilers in which steam is generated. The energy of expanding steam is then changed into electrical or mechanical energy. These forms of energy drive the machines of industry. Of course, industry secures energy from other sources, such as hydro-electricity or oil, but at the present time coal is by far the most important source of power.

It is from coal that coke is produced and this substance is essential for the production of steel from iron ore. Steel is necessary to make the machines for our modern factories, and so coal aids in the production of machines as well as being a source of energy to drive them. Thus, it is evident that the industrial prosperity of a nation depends to a large extent upon that nation's supply of this important mineral.

It has been estimated that the world's annual production of coal is about fifteen thousand million tons, and it is said that at the present rate of consumption, the earth's coal supply will be exhausted in five thousand years.

(b) *The Origin of Coal.* Coal has been formed from the luxurious vegetable growth of early geological ages. This vegetable matter, consisting of compounds chiefly of carbon, hydrogen and oxygen, was subjected to tremendous pressures and high temperatures in a limited supply of air. Under these conditions, the plant material was decomposed very slowly and after millions of years it was converted into coal. This process is called *carbonization*, because the slow changes by which coal was formed resulted in the partial liberation of hydrogen and oxygen, which were present in the original plants; so, as time passed, the percentage of carbon increased in the material.

Geologists tell us that the conditions most favourable to the formation of coal are found in fresh-water lakes bordered by flat, marshy land, on which an abundance of vegetation grows. The plants grow, decay and grow again, pushing their way out into the lake and gradually building up on the bed a mass of *peat*, which is the first stage in the development of coal. Gradually the mass hardens, first forming *lignite* or brown coal. As hundreds of thousands of years pass, the layers of peat are buried by masses of clay and sand, and so the peat through heat, pressure and chemical action becomes first *bituminous* or soft coal, and then *anthracite* or hard coal (Welsh and Pennsylvania).

which contains the highest percentage of carbon (about 85 per cent). Scientists have estimated that the coal which is now being taken from the mines, was deposited forty million to one hundred and fifty million years ago.

(2) COKE. When bituminous or soft coal is heated, out of contact with air, many gaseous products are given off, and a residue, containing all the mineral matter of coal, but composed chiefly of free carbon, is left behind. This solid material is known as *coke* and this process is called *destructive distillation.* During the changing of coal into coke, many of the complex carbon compounds, which are present in coal and which contain the elements carbon, oxygen, nitrogen and hydrogen, are decomposed by heat into simpler and more readily volatile substances. These volatile materials are distilled from the coal, and many of them are very useful as starting substances in the synthesis of important industrial chemicals. *Destructive distillation may be defined as a process in which a substance is decomposed by heat, out of contact with air, and the resulting gases condensed.*

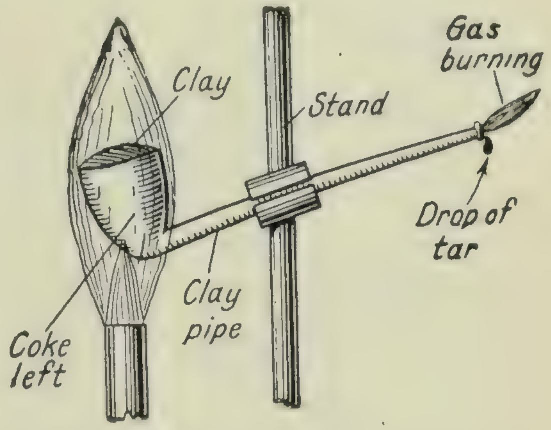


FIG. 80—HEATING COAL OUT OF CONTACT WITH AIR

Formerly coke was produced entirely in beehive ovens in which the coal was loosely placed in the oven and heated in a limited supply of air. Part of the coal burned and supplied enough heat to drive off the volatile substances from the unburned fraction. In this process the volatile materials, made up of coal gas (consisting chiefly of carbon monoxide, hydrogen, methane and other hydrocarbons), ammonia, and coal tar, were allowed to burn at the top of the oven. This was very wasteful. Now-a-days, in most countries, a different type of coking oven is used. It is known as a by-product coke oven. In this method the coal is heated in retorts and the volatile matter is collected. The coke remains in the retort. The ammonia gas is an important by-product of this process as well as the coal tar from which many materials, used in the manufacture of dyes, drugs, plastics and other chemicals, are secured by further distillation of the tar.

Coke is a black solid, somewhat porous in character. Its properties vary, however, with the nature of the coal from which it is produced. It usually contains from 5 to 20 per cent of mineral material, and burns with intense heat, but with hardly any flame and with no smoke. In addition to its use as a fuel, it is used to prepare water gas. However, its chief use is in metallurgy where it acts as a *reducing agent* to free metals, especially iron, from oxygen. The chief ore of iron found on this continent is haematite, ferric oxide, Fe_2O_3, and it is heated with coke and other substances in huge furnaces, known as blast furnaces. In these furnaces the chief chemical change taking place is the reduction of the iron ore by the coke according to the following equation:

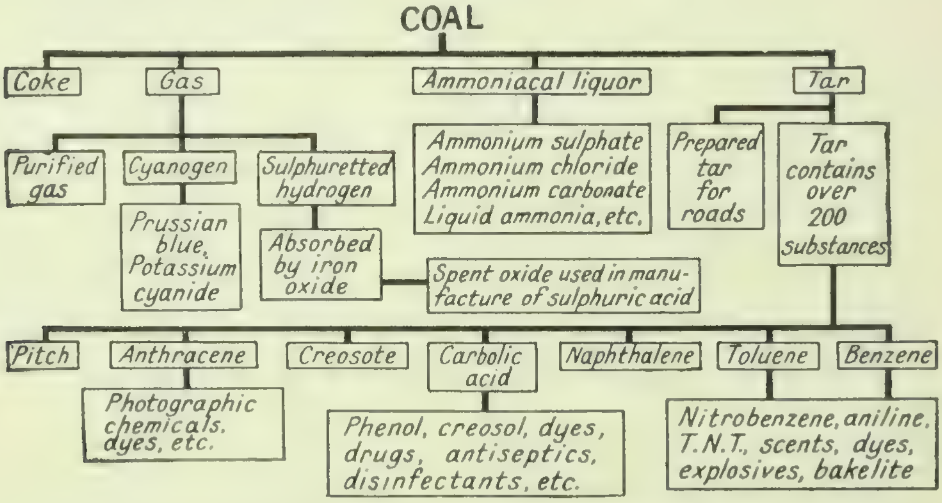

COAL
Coke
Gas
Ammoniacal liquor
Tar
Purified gas
Cyanogen
Sulphuretted hydrogen
Ammonium sulphate
Ammonium chloride
Ammonium carbonate
Liquid ammonia, etc.
Prepared tar for roads
Tar contains over 200 substances
Prussian blue, Potassium cyanide
Absorbed by iron oxide
Spent oxide used in manufacture of sulphuric acid
Pitch
Anthracene
Creosote
Carbolic acid
Naphthalene
Toluene
Benzene
Photographic chemicals, dyes, etc.
Phenol, creosol, dyes, drugs, antiseptics, disinfectants, etc.
Nitrobenzene, aniline, T.N.T., scents, dyes, explosives, bakelite

FIG. 81—THE CHIEF DERIVATIVES OF THE BY-PRODUCTS OF GAS MANUFACTURE

$$\underset{\text{(ferric oxide)}}{Fe_2O_3} + \underset{\text{(coke)}}{3\,C} \longrightarrow \underset{\text{(iron)}}{2\,Fe} + \underset{\text{(carbon monoxide)}}{3\,CO}\uparrow$$

It is this property of coke to remove the oxygen from the iron, with which it is combined in nature, that makes possible our so-called "Steel Age."

(3) WOOD CHARCOAL. Wood charcoal is produced by the destructive distillation of wood. The old method, called charcoal burning, in which piles of short lengths of wood were covered with earth and the wood was burned slowly, was very wasteful because all the gaseous products escaped into the air and were lost. In the modern charcoal plant, iron cars are loaded with hard woods and pushed, on a track, into a large retort, which is heated by fires underneath it. (See Fig. 82.) The volatile products escape, through pipes in the top of the retort, into condensers. The liquid which condenses is known as *pyroligneous*

acid. This liquid, when distilled can be separated into three very important liquids, namely, *methyl* (*wood*) *alcohol*, *acetic acid*, and *acetone*. After the volatile material has been driven off from the wood, the retort is allowed to cool, and the cars containing the charcoal are run out of the retort into air-tight cooling chambers, their places in the retort being taken by other cars loaded with wood. By means of this process, some factories convert 20 cords of wood into charcoal at one time, one cord of hardwood producing about 1000 lbs. of charcoal.

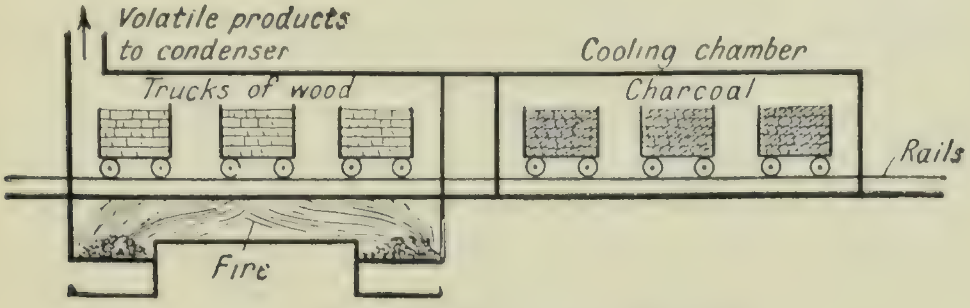


FIG. 82—MAKING WOOD CHARCOAL

Due to its porous nature, wood charcoal is very light and it has the remarkable property of *adsorbing* large volumes of gases on the surfaces of its pores. *Adsorption* (*not absorption*) is chiefly a surface phenomenon, in which certain molecules are attracted and held on the surfaces of particles of the adsorbing agent. Because of its power of adsorbing gases charcoal is used in gas masks for protection against poisonous gases. The best charcoal for this purpose is prepared from cocoanut shells, peach pits, the shells of nuts, or sugar. The masks are fitted to the face in such a way that all inhaled air must pass through a light metal box (canister) fitted with layers of various materials, the chief of which is charcoal. These substances either adsorb or combine with the poisonous gases. Gas masks are also used to protect workers in certain industries from poisonous fumes and they are also used in mine rescue work. Sometimes firemen must use gas masks when fighting fires which produce dangerous fumes.

It has been discovered that the power of charcoal to adsorb can be greatly increased by heating it again either in air or in steam. Sometimes catalysts are also added to it. Such charcoal is called *activated charcoal* and this is the type used in gas masks. Charcoal is used to a limited extent as a fuel. However, its greatest use is to clarify and to decolorize certain liquids, such as sugar solutions, syrups, acids, vegetable oils and petroleum products. This use, of course, depends upon the power of charcoal *to adsorb* the coloured impurities from the liquids.

(4) ANIMAL CHARCOAL. Animal charcoal, or bone-black, is produced by the destructive distillation of the bones of animals. Bones contain a very high percentage of mineral matter, about 60 per cent, which consists chiefly of calcium phosphate, $Ca_3(PO_4)_2$. Analysis shows that animal charcoal contains only about ten per cent of carbon. Its chief use is in the sugar refinery. Crude sugar has a yellow or brown colour. This colour is removed by dissolving the sugar in water and filtering the coloured solution through beds of bone-black. The coloured impurities of the sugar solution are adsorbed by the animal charcoal and a clear liquid obtained on filtration. When the filtrate is evaporated a pure white crystalline product is obtained. Animal charcoal is also used to clarify oils.

(5) LAMPBLACK. This form of carbon is often called carbon black. It is made by burning natural gas or oils in a limited supply of air. The highest quality is made from natural gas. When the supply of oxygen is limited, incomplete combustion occurs and burning produces a smoky flame due to the small particles of unburned carbon in it. This flame is directed upon moving metal surfaces on which the soot, or lampblack, is deposited. It is a very fine black powder, which consists almost entirely of pure carbon. Its chief use is in the manufacture of automobile tires and other rubber articles. Much carbon black is used in the manufacture of the following: printer's ink, typewriter ribbons, India ink, carbon paper, black enamel, black paint, phonograph records, and polishes for shoes and stoves.

5. Properties Common to all Forms of Carbon

The various forms of carbon described above differ in many respects, such as hardness, density, crystalline form and degree of purity. However, there are certain properties which are common to all the forms of carbon and these will be tabulated below:

(1) They are all black or greyish black except the diamond.
(2) They are all solids at room temperature.
(3) They are all odourless.
(4) They are all tasteless.
(5) They are all insoluble in water and ordinary solvents.

(6) They are unchanged by most chemical reagents such as acids and alkalis.

(7) They all burn to produce either carbon dioxide, CO_2, when there is an excess of air,

$$C + O_2 \longrightarrow CO_2$$

or carbon monoxide, CO when the supply of air is limited.

$$2\ C + O_2 \longrightarrow 2\ CO$$

(8) They are all powerful reducing agents. Examples of this property are:

$$CO_2 + C \longrightarrow 2\ CO$$
$$2\ CuO + C \longrightarrow 2\ Cu + CO_2$$
$$Fe_2O_3 + 3\ C \longrightarrow 2\ Fe + 3\ CO$$

EXERCISES

1. Write a note on the importance of carbon.
2. How does carbon occur in nature?
3. (a) Why is carbon called an allotropic element?
   (b) Name the crystalline forms of carbon.
   (c) Make a list of the amorphous forms.
4. Write a note on the occurrence of diamonds.
5. Tabulate the chief properties of diamonds.
6. Discuss the uses of the diamond.
7. How are artificial diamonds produced?
8. Describe the Acheson Process. Illustrate by means of a labelled drawing.
9. Tabulate the properties and uses of graphite.
10. Discuss the industrial importance of coal.
11. Write a note on the origin of coal.
12. (a) Define the term destructive distillation.
    (b) Discuss carefully the application of this process to coal and wood, telling what the chief by-products are in each case.
13. Why is coke so important to our modern civilization?
14. Tabulate the chief properties and uses of wood charcoal.
15. Write short notes on the following: gas masks, activated charcoal, animal charcoal, adsorption, and lampblack.
16. Tabulate the properties which are common to all forms of carbon.

CHAPTER XXII

CARBON DIOXIDE

1. Occurrence

(1) BURNING OF FUELS. Carbon dioxide is the gas produced whenever carbon or any of the common fuels, all of which contain carbon, burn in oxygen or air.

(2) A PRODUCT OF RESPIRATION. One of the essential life processes in animals is the slow combination of the oxygen, taken in by the lungs, with the carbon in the food which has been taken in by the body and digested. This reaction gives off heat which keeps the body warm and it also supplies the muscular energy needed to do work. The products of this body combustion, carbon dioxide and water vapour, are exhaled with each breath. Analysis of the exhaled breath shows that it contains 37 parts by volume of carbon dioxide in 1000 parts of exhaled air.

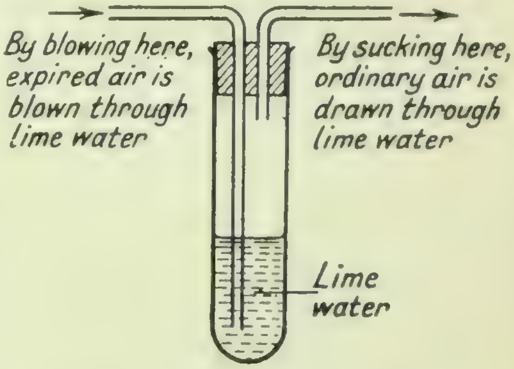

By blowing here, expired air is blown through lime water
By sucking here, ordinary air is drawn through lime water
Lime water

FIG. 83—CARBON DIOXIDE IN OUR BREATH

(3) IN THE AIR. Carbon dioxide is present in the air to the extent of about 3 parts by volume in 10,000 parts of air. This relatively small amount is essential to the life of all plants; so,

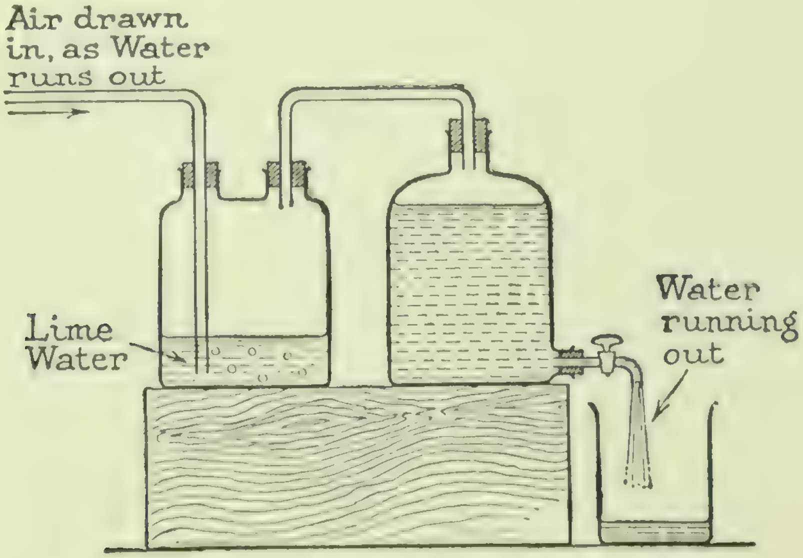
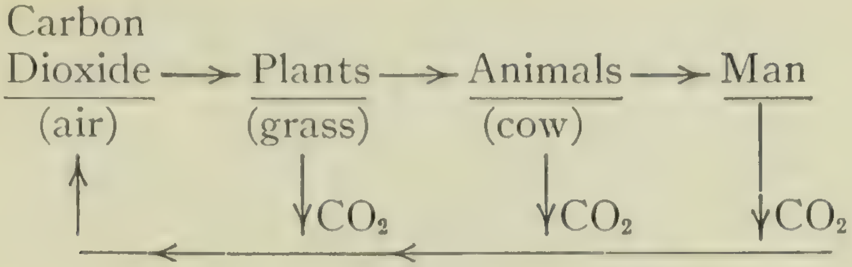


FIG. 84—PROVING CARBON DIOXIDE IS IN THE AIR

it indirectly serves to supply us with our food. The following diagram shows the *carbon cycle* in nature.



(4) FERMENTATION. Carbon dioxide is also formed in a process known as fermentation. The following word equation gives a general idea of this important process.

Sugar solution + Yeast ⟶ Alcohol + Carbon Dioxide

(5) DECAY OF PLANTS AND ANIMALS. When a plant or an animal dies, its body decays and one of the chief products of this process is carbon dioxide.

(6) VOLCANOES. Carbon dioxide is often present in the gases given off by volcanoes.

(7) CREVICES IN THE EARTH. It is well known that carbon dioxide escapes through openings in the earth's crust. In a cave near Naples, enough carbon dioxide issues from the cracks in its floor to form a layer from two to three feet deep from the bottom. If a man and a small dog walk through the cave, while the dog quickly becomes unconscious, and soon dies if not rescued, the man, whose head is well above the layer of gas, feels no bad effects. This cave, because of its fatal effect on dogs, is called Grotto del Cane, which means the "cave of the dog." The same phenomenon occurs in Death Valley in Java, where it has been reported that the whole of the bottom of the valley is covered with the skeletons of human beings, animals, and birds which have been overcome in the atmosphere of carbon dioxide.

2. Preparation

(1) BURN CARBON IN AIR OR OXYGEN.

$$C + O_2 \longrightarrow CO_2$$

This is sometimes used as a commercial method of producing the gas by burning coke in an abundant supply of air.

(2) BY THE ACTION OF AN ACID ON A CARBONATE. The usual laboratory method of preparing carbon dioxide is by the action of dilute hydrochloric acid on limestone or marble. Both

of these substances are almost completely composed of the compound, calcium carbonate, which has the formula $CaCO_3$.

$$\underset{\text{calcium carbonate}}{CaCO_3} + \underset{\text{hydrochloric acid}}{2\,HCl} \longrightarrow \underset{\text{calcium chloride}}{CaCl_2} + \underset{\text{carbonic acid}}{H_2CO_3}$$

$$\underset{\text{carbonic acid}}{H_2CO_3} \longrightarrow \underset{\text{water}}{H_2O} + \underset{\text{carbon dioxide}}{CO_2\uparrow}$$

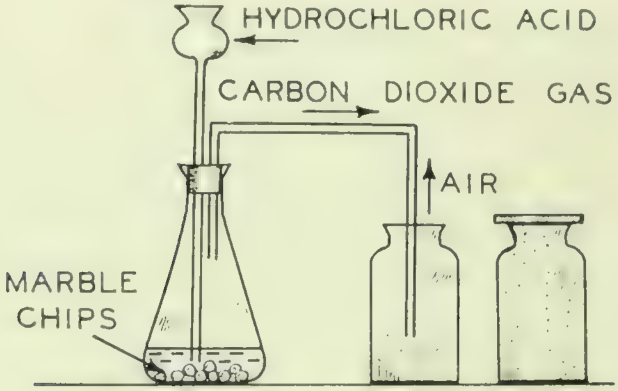


Fig. 85—The Usual Laboratory Preparation of Carbon Dioxide by the Action of Hydrochloric Acid on Marble Chips

The carbonic acid, H_2CO_3, which is formed by the double decomposition reaction between the acid and the carbonate, is very unstable and breaks up at once into carbon dioxide and water. Thus, the complete reaction may be written in one equation as follows:

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + CO_2\uparrow$$

(3) Heating Carbonates, except those of sodium and potassium. One of the most abundant carbonates found in nature is calcium carbonate, limestone. When this substance is heated calcium oxide, CaO, and carbon dioxide are produced.

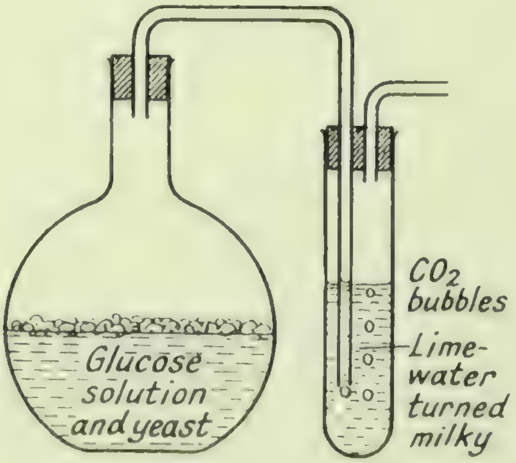


Fig. 86—Carbon Dioxide from the Fermentation of Sugar

Calcium oxide is known in commerce as quicklime and it is a very important material in the building trades.

$$\underset{\substack{\text{calcium}\\\text{carbonate}}}{CaCO_3} \longleftarrow \underset{\substack{\text{calcium}\\\text{oxide}}}{CaO} + CO_2\uparrow$$

(4) FERMENTATION. Carbon dioxide is produced in certain fermentations, such as that of the sugar glucose to ethyl alcohol according to the following equation:

$$\underset{\text{glucose}}{C_6H_{12}O_6} \longrightarrow 2\ \underset{\substack{\text{ethyl}\\\text{alcohol}}}{C_2H_5OH} + 2\ CO_2\uparrow$$

3. Physical Properties

(1) Carbon dioxide is a *gas* at ordinary temperature and pressure.

(2) It is *colourless.*

(3) The gas is also *odourless.*

(4) Carbon dioxide is about 1.5 times *heavier than air.*

(5) At 15° C. and under one atmosphere of pressure, *one litre of water dissolves about one litre of the gas.* Under several atmospheres of pressure more carbon dioxide will go into solution. This fact is made use of in the soft drink industries.

(6) By applying sufficient pressure to carbon dioxide gas (59 atmospheres at 20° C.) at ordinary temperatures, it may be condensed to a *liquid.* This liquid is an article of commerce and it is sold in steel cylinders.

(7) When the liquid carbon dioxide is allowed to escape from such a cylinder, part of the gas evaporates quickly and removes so much heat that the rest is frozen to a snow-like solid, known as "dry ice." This substance evaporates slowly without melting, keeping at a temperature of about −79° C. as long as it lasts.

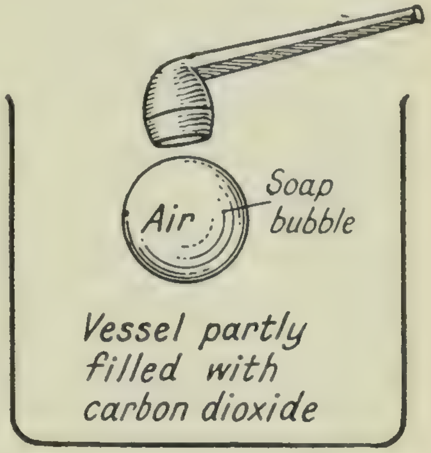


FIG. 87—AIR BUBBLE FLOATING ON CARBON DIOXIDE, SHOWING THAT THE GAS IS HEAVIER THAN AIR

4. Chemical Properties

(1) Carbon dioxide WILL NOT BURN.

(2) IT DOES NOT SUPPORT THE COMBUSTION OF MOST SUBSTANCES.

A few vigorous reducing agents, such as magnesium and sodium,

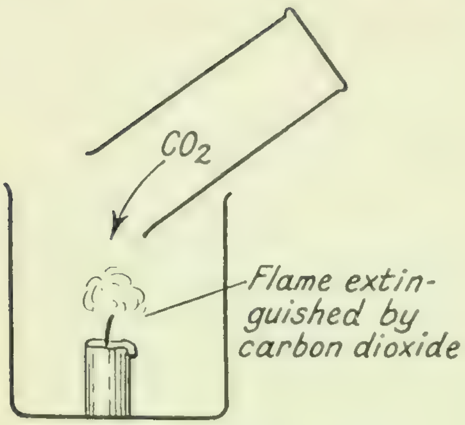


FIG. 88—POURING CARBON DIOXIDE ON A FLAME

are capable of removing the oxygen from carbon dioxide. These substances will, therefore, burn in it. Thus, an ignited strip of magnesium ribbon will continue to burn in an atmosphere of carbon dioxide according to the equation:

$$2\ Mg + CO_2 \longrightarrow 2\ MgO + C$$

The most familiar reducing agent for carbon dioxide is carbon and the equation is as follows:

$$CO_2 + C \longrightarrow 2\ CO$$

This reduction takes place whenever carbon dioxide (in the absence of oxygen) passes over hot carbon.

(3) CARBON DIOXIDE COMBINES WITH WATER TO FORM CARBONIC ACID. This is produced by the reaction:

$$H_2O + CO_2 \rightleftharpoons \underset{\text{carbonic acid}}{H_2CO_3}$$

Due to the above reaction, carbon dioxide is often called "carbonic acid gas" in commerce.

(4) COMBINES WITH BASES (ALKALIS) TO FORM A GROUP OF COMPOUNDS CALLED CARBONATES. For example, when carbon dioxide is bubbled into a solution of lime-water, $Ca(OH)_2$, a part of the gas dissolves, forming carbonic acid. This then reacts with the calcium hydroxide as follows:

$$\underset{\substack{\text{carbonic}\\\text{acid}}}{H_2CO_3} + \underset{\substack{\text{calcium}\\\text{hydroxide}\\\text{(lime-water)}}}{Ca(OH)_2} \longrightarrow \underset{\substack{\text{calcium}\\\text{carbonate}}}{CaCO_3\downarrow} + 2\ H_2O$$

Calcium carbonate is only slightly soluble in water and precipitates from the solution as a white suspension. This reaction is used as a chemical test for carbon dioxide.

(5) THE EFFECT ON THE HUMAN BODY. A person would be suffocated in an atmosphere of carbon dioxide due to lack of oxygen, but the gas is not poisonous. Small amounts of carbon dioxide stimulate the nerve centres that control respiration; so, about seven per cent carbon dioxide is used with oxygen in pulmotors.

5. Uses

(1) PLANT FOOD. All green plants need carbon dioxide; they would not grow without it. This use of carbon dioxide is

so important that it will be discussed in detail in the next section of this chapter under the heading of *photosynthesis*.

(2) BAKING. In the baking of bread and cake, carbon dioxide is generated in the dough, and forces its way through the mass, making it light and porous.

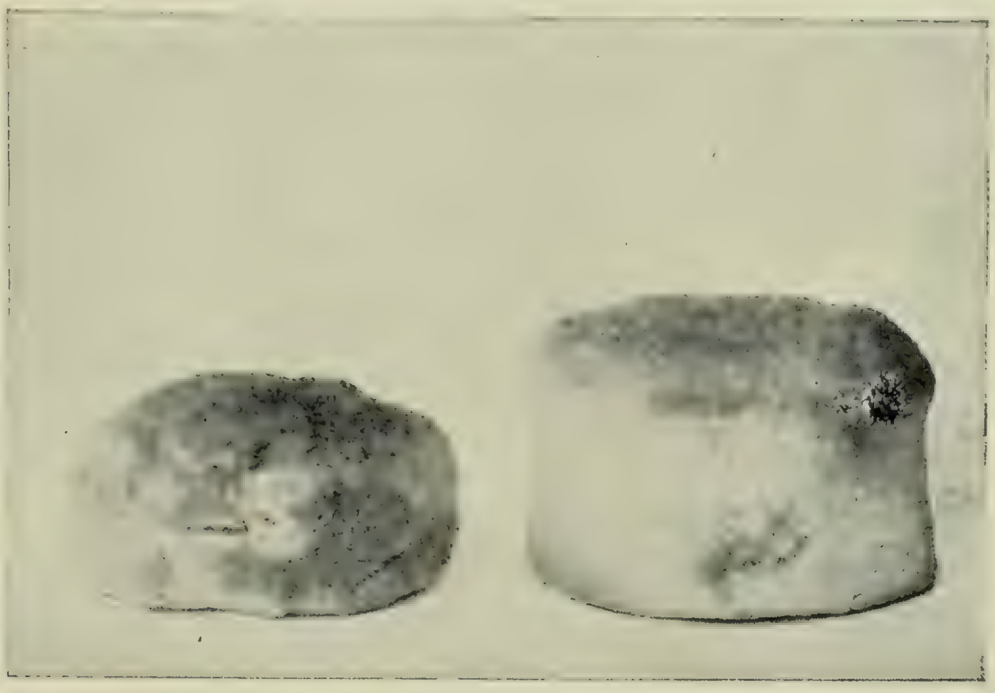


FIG. 89

Two cakes made from identical recipes, except that the one on the right had one teaspoonful of baking powder added, which produced enough carbon dioxide in baking to make it rise more. The carbon dioxide also makes the cake light and porous.

(3) IN MANUFACTURE OF WASHING AND BAKING SODA. Large quantities of carbon dioxide are used in the manufacture of washing soda (sodium carbonate, $Na_2CO_3 . 10H_2O$) and baking soda ($NaHCO_3$) by the Solvay process.

(4) IN MANUFACTURE OF SOFT DRINKS. Much of the gas is used every year in producing carbonated ("soda") water and soft drinks, which are solutions of sugar and various flavours containing carbonic dioxide or carbonic acid under pressure.

(5) FIRE EXTINGUISHERS. The chemical property possessed by carbon dioxide of not supporting

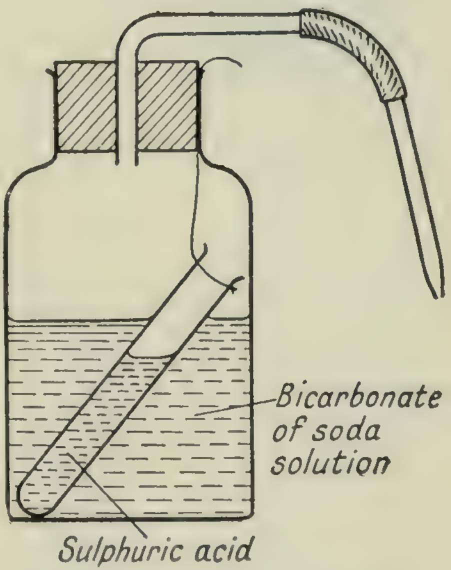
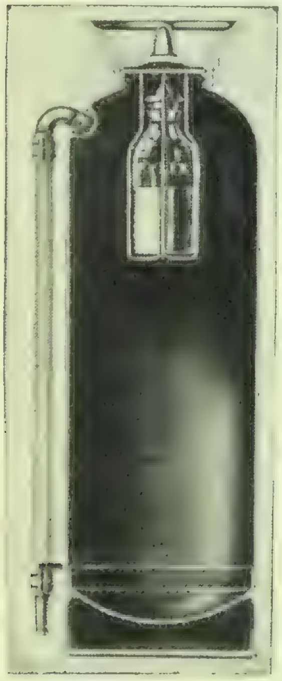


FIG. 90—A MODEL FIRE EXTINGUISHER

combustion is often made use of in extinguishing fires. A common type of extinguisher, which contains a solution of sodium bicarbonate, is shown in Fig. 91. A bottle containing concentrated sulphuric acid is held in place near the top. When not in use the container is kept in an upright position. In case of a fire the cylinder is turned upside down, and the stopper then drops out of the acid bottle. The following chemical reaction then takes place between the sulphuric acid and sodium bicarbonate:

$$2\ NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ H_2O + 2\ CO_2\uparrow$$

Much pressure develops in the container, and the solution becomes saturated with the gas. The pressure forces the solution out through the nozzle. The carbon dioxide, which is carried by the escaping solution, partially excludes the oxygen of the air and assists the water in putting out the fire. Such extinguishers are very effective but somewhat heavy to handle. The concentrated sulphuric acid gradually absorbs water from the bicarbonate solution, and in time the acid becomes quite dilute. For this reason, fresh acid must be put into them about once a year as the weak acid is ineffective and the extinguisher would not work properly in case of a fire.



Courtesy of LaFrance Fire Engine and Foamite Ltd.

Fig. 91

The Cross-Section of a Soda-Acid Extinguisher

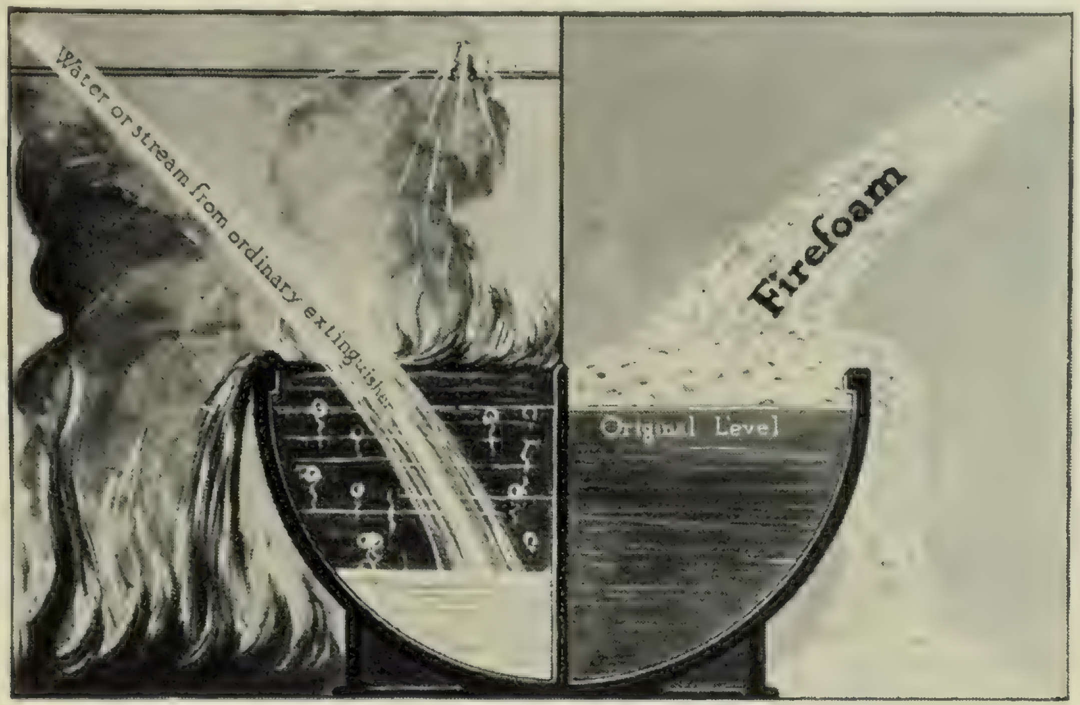
The glass bottle which has a loose stopper, contains sulphuric acid; a solution of sodium bicarbonate is placed in the main cylinder. It is operated by turning the bottom up.

Special fire extinguishers made for fighting oil and gasoline fires contain a foam producing material. When this substance is used, the fire is covered with a heavy layer of foam consisting of carbon dioxide bubbles. This blanket of gas prevents air from coming in contact with the burning substance, and so puts out the fire. One of the best-known extinguishers of this type is sold under the trade name of "Foamite." The inner container of the extinguisher contains a solution of aluminum sulphate, $Al_2(SO_4)_3$. The outer cylinder contains a solution of sodium bicarbonate, $NaHCO_3$, and licorice. When these two solutions are brought together the following reaction takes place:

$$Al_2(SO_4)_3 + 6\ NaHCO_3 \longrightarrow 3\ Na_2SO_4 + 2\ Al\ (OH)_3\downarrow + 6\ CO_2\uparrow$$

The licorice, the gelatinous precipitate of aluminum hydroxide, $Al(OH)_3$, and the carbon dioxide make up the foam, which is so effective in fighting oil fires.

Liquid carbon dioxide fire extinguishers are also available such as the one shown in Fig. 94.


Water or stream from ordinary extinguisher
Firefoam
Original Level

Courtesy of LaFrance Fire Engine and Foamite Ltd.

FIG. 92—SMOTHERING AN OIL FIRE

Note how the foam which is lighter than the oil but heavier than air, excludes the atmospheric oxygen. Compare with the effect of the water, which is heavier than the oil.

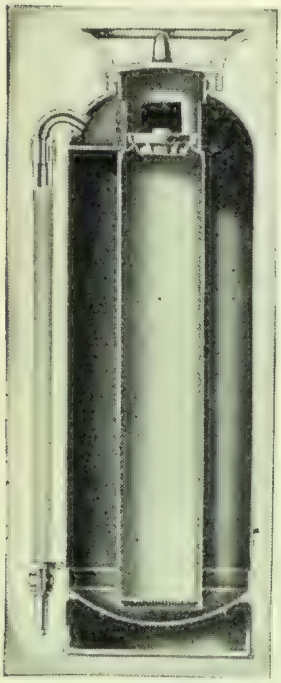
(6) WHITE LEAD. Carbon dioxide is used in the manufacture of white lead, which is an important component of many paints.

(7) REFRIGERANT. Carbon dioxide in the solid state, known as dry ice, is used to a considerable extent in the shipment of perishable foods, such as fruit, fish, and meat, and to preserve ice cream.

(8) IN MEDICINE. Carbon dioxide is also mixed with the oxygen (7 per cent dioxide and 93 per cent oxygen) which is given to persons suffering from certain diseases of the lungs, such as pneumonia, and in cases of asphyxiation. The presence of this amount of carbon dioxide (7 per cent) stimulates the nerve centres which control respiration.

(9) IN AVIATION. Carbon dioxide has been found to be very useful in the field of aviation. If a plane is disabled and must make a forced landing on water, carbon dioxide gives the

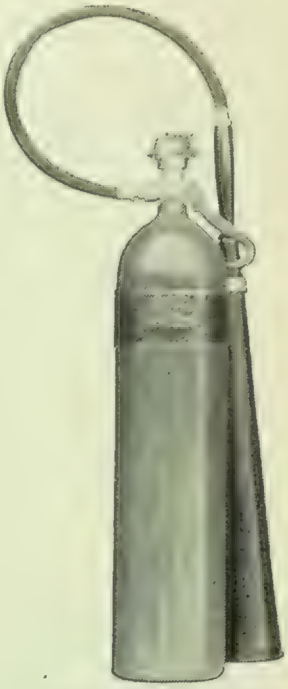
pilot, crew, and passengers, a good chance of being rescued. All planes flying over large bodies of water carry a rubber life raft which is automatically inflated with carbon dioxide as soon as the airplane lands on the water. Other important uses of this gas in aviation are described in books on that subject.



Courtesy of LaFrance Fire Engine and Foamite Ltd.

FIG. 93—THE CROSS-SECTION OF A PORTABLE FOAM-PRODUCING EXTINGUISHER

The inner canister, which has a loose stopper, contains a solution of aluminum sulphate; a solution of sodium bicarbonate and a foaming agent is placed in the main cylinder. It is operated by turning the bottom up.



Courtesy of LaFrance Fire Engine and Foamite Ltd.

FIG. 94—A LIQUID CARBON DIOXIDE TYPE FIRE EXTINGUISHER

This hand portable type is carried close to the fire, and when the *valve is opened* the heavy gas pours out through the funnel.

6. Photosynthesis

Scientists have been attempting for many years to find out how plants manufacture such complex materials as cellulose, starches, sugars, fats, proteins, and vitamins. It has been found that every plant contains a small factory, in which there is built from the raw materials these products which are so essential to man's existence.

It is in the green leaf that this wonderful process takes place. The raw materials consist of carbon dioxide, water and minerals from the soil. The carbon dioxide enters the leaf through very small openings on the surface. The minerals, used in this process, must be soluble in the water which comes up to the green leaf through the roots and stem from the soil. Chlorophyll, the green colouring matter in plant leaves, plays an important part in this manufacturing process. Sunlight, too, is employed, furnishing the energy which converts the raw materials into compounds such as starch and cellulose. The presence of chlorophyll is always necessary to the process, which is known as *photosynthesis*, coming from the Greek word meaning "to build up by means of light."

Directly or indirectly all life is dependent on these minute plant factories. Here the plant produces its own food, and from the factory this food is sent to other parts of the plant for storage. Animals live on plants, and man in turn requires the meat of animals in his diet. Thus, man's existence depends upon the stores of food which are built through the process of photosynthesis. Furthermore, we are dependent on it for wood, coal and oil. On these, in turn, depend steam power, motor transportation, and other important materials necessary in our modern civilization.

For many years scientists have attempted to duplicate in the laboratory this process which is carried on in the green leaf, but as yet attempts to do so on a practical scale have met with failure.

EXERCISES

1. Answer the following questions concerning carbon dioxide:
    (a) By what other name is it known?
    (b) Name five natural sources of the gas.
    (c) Account for the fact that it can be poured from one vessel into another like water.
    (d) What property of the gas is used in making soda water?
    (e) Write the equation for the usual laboratory preparation of this gas. Name all chemicals involved.
2. Name six important commercial uses of carbon dioxide.
3. Why does soda water effervesce when the bottle is uncorked?
4. Tell what takes place under the following conditions:
    (a) When carbon dioxide is passed into water.
    (b) When it is poured over a flame.
    (c) When it is passed into lime-water.
5. (a) Give the names and formulas of all gases which we have studied so far.
    (b) Tell how you could distinguish each of them.
6. How could you show that carbon dioxide is contained in the air and breathed out from the lungs?
7. Write a note on photosynthesis, stressing the importance of it in our daily lives.

CHAPTER XXIII

CARBON MONOXIDE

1. Preparation

(1) BY BURNING CARBON IN A LIMITED SUPPLY OF AIR. Carbon monoxide does not occur in nature, but it is produced when carbon (or a material containing it) is burned in a limited supply of air or oxygen. The equation for this reaction is as follows:

$$2\ C + O_2 \longrightarrow 2\ CO$$

(2) BY PASSING CARBON DIOXIDE OVER HIGHLY HEATED CARBON. The equation for this reaction is as follows:

$$CO_2 + C \longrightarrow 2\ CO$$

The gas is formed in this way in a hot coal or coke fire and the blue flame which is observed in these fires is due to the burning of the carbon monoxide. At the bottom of the fire, just above the grate, the coal burns well and carbon dioxide is formed there. This gas is carried upwards by the draught of the burning fuel through the red-hot coals (carbon) in the central region of the fire where the oxygen supply is limited. Here the carbon dioxide is reduced to carbon monoxide according to the above equation. Upon reaching the top of the fire the carbon monoxide comes in contact with plenty of oxygen and it burns to produce carbon dioxide. (See Fig. 95.)

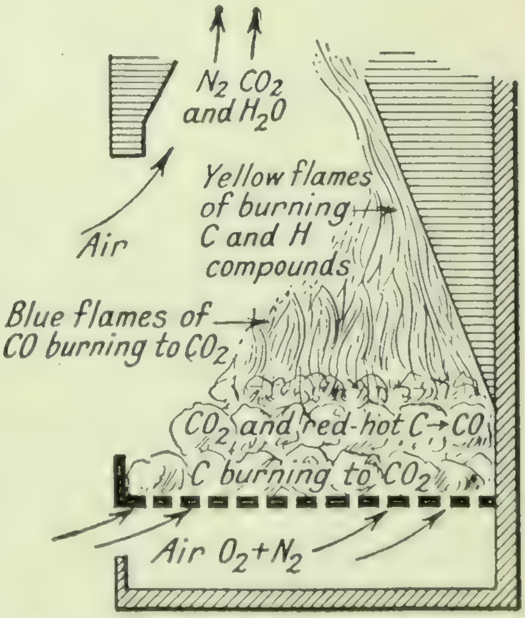

N_2 CO_2 and H_2O
Yellow flames of burning C and H compounds
Air
Blue flames of CO burning to CO_2
CO_2 and red-hot C → CO
C burning to CO_2
Air O_2+N_2

FIG. 95—CARBON MONOXIDE FLAME IN A COAL FIRE

$$2\ CO + O_2 \longrightarrow 2\ CO_2$$

(3) BY THE ACTION OF WARM CONCENTRATED SULPHURIC ACID ON FORMIC ACID. The equation for the reaction is:

$$HCOOH \longrightarrow H_2O + CO\uparrow$$

The sulphuric acid takes no part in the reaction but it absorbs the water which is produced.

2. Physical Properties

(1) Carbon monoxide is a *gas* under ordinary conditions.

(2) It is a *colourless* gas.

(3) This gas is *odourless*, which increases its dangerous nature.

(4) Carbon monoxide is *slightly lighter than air.* One litre weighs 1.25 grams.

(5) It is *very slightly soluble* in water.

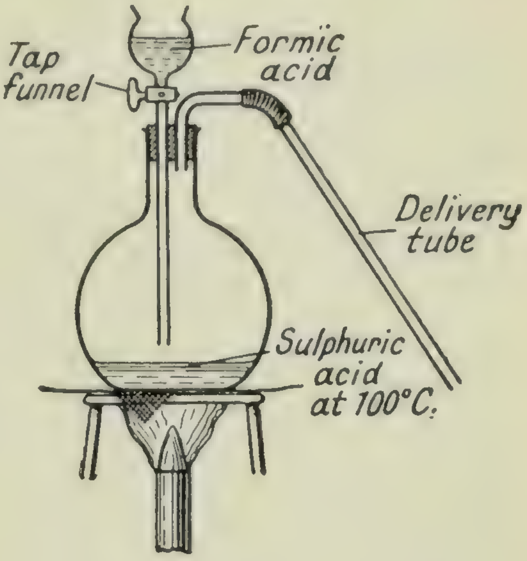


Fig. 96—Preparation of Carbon Monoxide

3. Chemical Properties

(1) This gas *does not support combustion.*

(2) It *burns* in air with a pale blue flame. The reaction is:

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

(3) Carbon monoxide is a *good reducing agent* and this property is made use of to a considerable extent in industry. For example, it is the chief reducing agent in the blast furnace, converting the iron oxide of iron ore into free iron according to the following equation:

$$Fe_2O_3 + 3\,CO \longrightarrow 2\,Fe + 3\,CO_2\uparrow$$

Another illustration of its reducing power is the conversion of cupric oxide into free copper, when the gas is passed over the hot oxide. The equation for this reaction is:

$$CuO + CO \longrightarrow Cu + CO_2\uparrow$$

(4) Very Poisonous. Often we read of accidents caused by the escape of carbon monoxide gas from the exhaust of motor engines or from furnace pipes. This gas is very poisonous. Since is is odourless, it often overcomes victims so quickly that they seldom have time to escape from the fumes.

The very poisonous nature of the gas is due to its action on the blood, where it displaces the oxygen in the haemoglobin of the red corpuscles, forming a stable compound. Thus, the haemoglobin is prevented from doing its normal task of carrying oxygen from the lungs to oxidize materials in all parts of the body. Death occurs when the blood loses its power to absorb and carry a sufficient supply of oxygen. In other words, death results from internal suffocation.

It is estimated that one volume of carbon monoxide in 800 volumes of air is fatal when breathed for half an hour, while much smaller quantities are known to produce unpleasant symptoms, such as a severe headache, if inhaled for any length of time. Small cars, travelling at fifteen miles per hour, are said to give off about 40 cu. ft. of carbon monoxide per hour, while large cars give off as much as 180 cu. ft. of the gas in one hour. Thus, in large cities the air always contains small amounts of the gas, and much attention has been given in some centres to purifying the air, especially in tunnels and underground railways. This is done by passing the air over a substance known as *hopcalite* (a mixture of metallic oxides, such as MnO_2, CuO, Co_2O_3, and Ag_2O), which changes the carbon monoxide, by means of catalytic action, into harmless carbon dioxide.

As birds are very sensitive to carbon monoxide rescue crews in mines sometimes take canaries in cages with them after an explosion in which this gas is believed to have been released. Recently a *chemical test* has been devised to detect the presence of carbon monoxide. Charcoal in the ordinary gas mask does not adsorb carbon monoxide; so, special gas masks, containing hopcalite, are used in coal mines for rescue work.

4. Uses of Carbon Monoxide

(1) As a Fuel. Carbon monoxide's most important use is as a fuel. It is not used by itself but in mixtures of gases such as coal gas, producer gas, water gas, and blast-furnace gas.

(2) Industrial Reducing Agent. Carbon monoxide is used to a considerable extent in metallurgical work for the reduction of the oxides of many of the metals, such as iron, copper, and zinc. For example, the gas is the chief reducing agent in the blast furnace, where pig iron is produced.

(3) To Prepare Wood Alcohol (Methyl Alcohol). Carbon monoxide is used in the production of synthetic methyl alcohol. In this process a mixture of carbon monoxide and hydrogen, at about 400° C., is passed over a catalyst, which usually consists of zinc oxide and finely divided (reduced) copper. The equation for this reaction is:

$$CO + 2\,H_2 \longrightarrow \underset{\text{(methyl alcohol)}}{CH_3OH}$$

(4) In Preparation of Phosgene. Carbon monoxide combines with chlorine in sunlight or in the presence of a catalyst to produce phosgene, which is a war gas and a chemical used in the manufacture of an important class of dyes. The equation for this preparation is:

$$\underset{\text{}}{CO} + \underset{\text{chlorine}}{Cl_2} \longrightarrow \underset{\text{phosgene}}{COCl_2}$$

EXERCISES

1. Discuss the reactions which occur in a coal fire. Illustrate your answer with a drawing.
2. Describe carefully the laboratory preparation of carbon monoxide. Illustrate your answer with a labelled diagram. Write the equation for the reaction.
3. Tabulate four physical and three chemical properties of carbon monoxide.
4. Discuss carefully the effect of carbon monoxide on the human body.
5. Write a note on the uses of carbon monoxide.
6. (a) What is hopcalite?
   (b) Discuss briefly some commercial uses of this substance.

CHAPTER XXIV

NITROGEN

1. Importance of Nitrogen

Nitrogen is an indispensable element, because all life depends upon it. While this is true, it is also a fact that neither animals nor plants, with the exception of certain families of bacteria, possess the power of taking nitrogen directly from the air, of which it makes up about four-fifths by volume. While nitrogen does not appear to play an active role in the air as does oxygen, it is essential; animal life in an atmosphere of pure oxygen would soon pass into an abnormal state and die.

2. Occurrence

(1) IN THE FREE STATE. Nitrogen occurs in the air uncombined with other gases and in enormous quantity. It has been calculated that there are 20,000,000 tons of nitrogen above each square mile of the earth's surface. Since there are 640 acres in a square mile, a farmer possessing this amount of land may lay claim to enough nitrogen to supply necessary nitrogen compounds to the whole world for fifty years at the present rate of consumption.

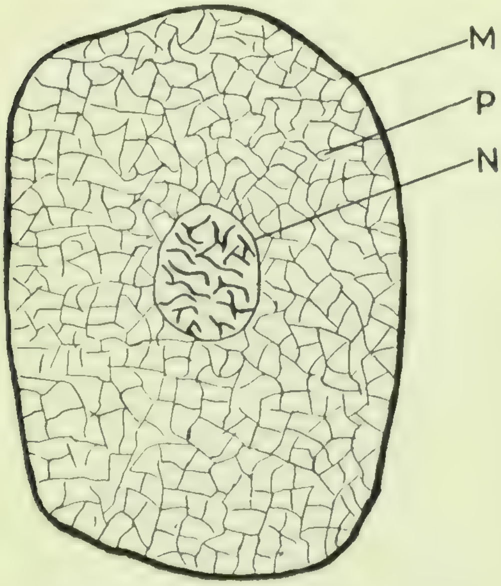


FIG. 97—A TYPICAL CELL
M, membrane; P, protoplasm, N, nucleus.

The great abundance of free nitrogen is due to its inertness under ordinary conditions and to the further fact that many nitrogen compounds are more or less unstable, and so tend to give up nitrogen to the air.

(2) IN THE COMBINED STATE. Nature cannot build a single cell without nitrogen which is present in all *proteins*. Proteins are necessary for the formation of protoplasm which, in turn, is the chief component of all living cells. Thus, the marvellous properties of living matter depend in part upon the presence of nitrogen.

Furthermore, nitrogen is an essential constituent of all commercial *explosives* such as guncotton and T.N.T. (trinitrotoluene).

Nitrogen is present in a group of important compounds known as *nitrates*. Potassium nitrate, or saltpetre, KNO_3, and sodium nitrate, or Chile saltpetre, $NaNO_3$, are good examples of nitrates. A very large deposit of sodium nitrate is found in a desert area in the mountains of Chile, along the Pacific coast of South America. The material removed from the deposit is called *caliche* and it is treated with water. The sodium nitrate, being very soluble in water, is washed away from the insoluble impurities in the caliche. The solution is then evaporated and the product so obtained is called *Chile saltpetre*.

Nitrogen is an essential constituent of the food which plants must obtain from the soil. In spite of its apparent inertness and lack of odour, colour, or taste, all life would sicken and die if deprived of nitrogen or nitrogenous compounds. Bountiful harvests and vigorous growth of grass, flowers and trees are obtained only when the soil contains proper nitrogenous *fertilizers*. Nitrogen, potassium, and phosphorus are the three essential chemical elements needed for plant growth; so, all good chemical fertilizers should contain these elements. The nitrogen present in these mixtures is usually in the form of nitrates or ammonium salts, such as sodium nitrate, $NaNO_3$, ammonium nitrate, NH_4NO_3, ammonium sulphate, $(NH_4)_2SO_4$, or ammonium phosphate, $(NH_4)_3PO_4$. In the manufacture of fertilizers large quantities of ammonia, NH_3, and nitric acid, HNO_3, are required.

In addition to being found in ammonia and nitric acid, nitrogen is an important constituent of the molecules of certain useful *drugs* and *medicines*. It is also present in many *commercial dyes*.

3. Preparation

(1) IN THE LABORATORY. (a) *From the Atmosphere.* Nitrogen can be prepared in the laboratory from the atmosphere by removing the oxygen of the air by means of some easily oxidized substance such as phosphorus, copper, hydrogen or carbon. In order to secure a reasonably pure sample of nitrogen, the products of the combustion must be either solids or gases which are quite soluble in water.

The method shown in Fig. 98 may be used when phosphorus is the oxidizing agent. The dense white smoke produced in this experiment is due to the formation of very fine solid particles of the compound phosphorus pentoxide. The equation for this reaction is:

$$\underset{\text{Phosphorus}}{P_4} + 5\ O_2 \longrightarrow \underset{\text{Phosphorus pentoxide}}{2\ P_2O_5}$$

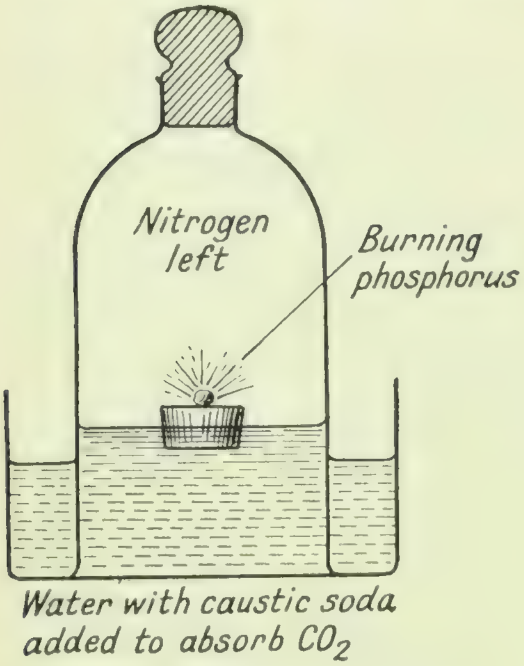


FIG. 98—NITROGEN FROM AIR

The pentoxide dissolves gradually in the water in the bell jar. The nitrogen remaining in the jar contains argon, carbon dioxide, and a small quantity of oxygen because the phosphorus stops burning before all the oxygen is used up. The carbon dioxide may be taken out by adding sodium hydroxide (caustic soda), NaOH, to the water. If some blue litmus solution is added to the water in the bell jar before the phosphorus is ignited, it will be observed shortly after the experiment has started that the litmus changes to a red colour. This change in colour indicates that an acid was formed during the experiment. It is phosphoric acid and is produced according to the following equation:

$$\underset{\text{Phosphorus pentoxide}}{P_2O_5} + 3\ H_2O \longrightarrow \underset{\text{Phosphoric acid}}{2\ H_3PO_4}$$

Another laboratory method of removing the oxygen from the atmosphere to leave behind atmospheric nitrogen is shown in Fig. 99. Air is passed through a bottle containing sodium

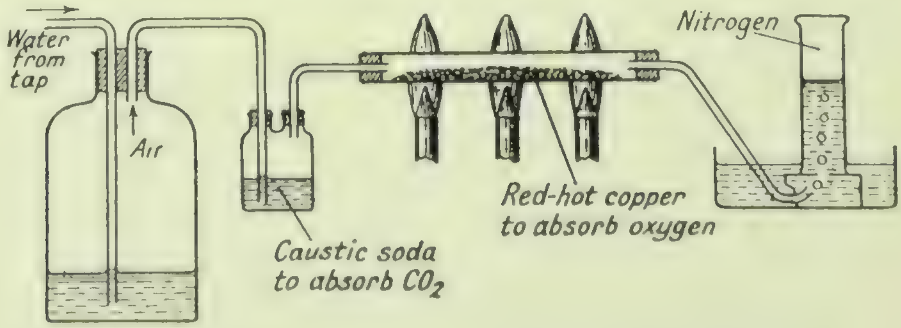

Water from tap
Air
Caustic soda to absorb CO_2
Red-hot copper to absorb oxygen
Nitrogen

FIG. 99—THE PREPARATION OF NITROGEN FROM THE AIR

hydroxide (caustic soda) to remove the carbon dioxide. It is then conducted through a tube which contains red-hot copper. The copper is changed to copper oxide according to the equation:

$$\underset{\text{copper}}{2\,Cu} + O_2 \longrightarrow \underset{\text{copper oxide}}{2\,CuO}$$

The nitrogen does not combine with the copper and is collected by the downward displacement of water.

Nitrogen prepared from the atmosphere is called *atmospheric nitrogen.* It is never pure because it contains carbon dioxide, water vapour and the inert gases.

(b) *From Chemical Compounds.* Small quantities of *pure* nitrogen can be readily prepared by gently heating a mixture of ammonium chloride, sodium nitrite, and water in a hydrogen generator and collecting the nitrogen by the downward displacement of water. The equation for this reaction is:

$$\underset{\substack{\text{ammonium}\\\text{chloride}}}{NH_4Cl} + \underset{\substack{\text{sodium}\\\text{nitrite}}}{NaNO_2} \longrightarrow \underset{\substack{\text{sodium}\\\text{chloride}}}{NaCl} + \underset{\substack{\text{ammonium}\\\text{nitrite}}}{NH_4NO_2}$$

Ammonium nitrite is very unstable and decomposes at once into nitrogen and water. The equation is:

$$\underset{\substack{\text{ammonium}\\\text{nitrite}}}{NH_4NO_2} \longrightarrow \underset{\text{nitrogen}}{N_2} + 2\,H_2O$$

If the chemicals used in the above preparation are pure, then the sample of nitrogen obtained would be pure. Nitrogen produced in this way is known as *chemical nitrogen.*

(2) COMMERCIALLY. The commercial method of preparing nitrogen from liquid air has already been described in the chapter on oxygen (see page 47). It will be recalled that air is changed to a liquid by the use of high pressures and low temperatures, the liquid being separated into oxygen and nitrogen by the process of fractional distillation. The boiling point of nitrogen is about—196° C., and that of oxygen is—183° C., under one atmosphere of pressure. Thus, the nitrogen boils off first, leaving oxygen behind as a liquid. Commercial nitrogen contains about one per cent of impurities, chiefly argon. However, this gas is so inert that it does not affect the usefulness of nitrogen to any marked extent.

4. Physical Properties

(1) Nitrogen is usually found as a *gas* but under certain conditions it can be converted to a liquid or to a solid.

(2) It is *colourless.*

(3) The gas is also *odourless.*

(4) Nitrogen is *slightly lighter than air,* one litre of the gas weighing 1.25 grams at S.T.P.

(5) It is only very slightly soluble in water; under standard conditions, 100 c.c. of water dissolves about 2.3 c.c. of nitrogen.

5. Chemical Properties

(1) In spite of the fact that the compounds of nitrogen are numerous, and many of them are very active, the element itself is relatively *inert.*

(2) *It does not support combustion or respiration.*

(3) Nitrogen *does not burn.*

(4) It is *not a poisonous gas* (we breathe it all the time).

(5) At high temperatures nitrogen *combines with oxygen* to form nitric oxide, NO. This oxide, in turn, when cooled to ordinary room temperatures, will combine with more oxygen of the air to form nitrogen dioxide, NO_2. These oxides have important industrial applications.

$$N_2 + O_2 \longrightarrow \underset{\text{nitric oxide}}{2\,NO}$$

$$2\,NO + O_2 \longrightarrow \underset{\text{nitrogen dioxide}}{2\,NO_2}$$

(6) At high temperatures and under suitable conditions nitrogen combines to form a group of compounds known as *nitrides.* Equations for the formation of a few of these substances are given below:

$$N_2 + 3\,H_2 \rightleftharpoons \underset{\text{ammonia}}{2\,NH_3}$$

$$\underset{\text{calcium}}{3\,Ca} + N_2 \longrightarrow \underset{\text{calcium nitride}}{Ca_3N_2}$$

$$\underset{\text{magnesium}}{3\,Mg} + N_2 \longrightarrow \underset{\text{magnesium nitride}}{Mg_3N_2}$$

6. Uses

(1) The chief commercial use of free nitrogen is in the preparation of *ammonia,* NH_3, by direct combination with hydrogen. The ammonia, in turn, is used in the manufacture of fertilizers and other compounds of nitrogen, especially nitric acid, HNO_3, which is necessary for the production of explosives, photographic films, lacquers, drugs, and dyes.

(2) Nitrogen is used to *fill certain kinds of electric light bulbs.* Because of its inertness it does not allow the white-hot filament in the lamp to oxidize.

(3) Large quantities of nitrogen are needed for purposes of *nitrogen fixation.* This term is applied to any process by which

the free nitrogen of the air is changed into nitrogen compounds. Since these compounds are essential to our existence, and since uncombined nitrogen is present in the air in such enormous quantities, chemists have devised several industrial methods of nitrogen fixation. Some of these will be discussed in the chapters on ammonia and nitric acid. Certain plants can fix the nitrogen of the air into compounds, which serve as food for plants, and this topic will now be discussed in some detail in the next section of this chapter.

7. Nitrogen Fixation by Plants

The free nitrogen of the air cannot be used by most plants. However, certain plants, called the *legumes*, can utilize the atmospheric nitrogen. The legume family includes peas, beans, alfalfa, and sweet clover. The roots of these plants have nodules, which look like very small potatoes on the roots of a potato plant, and in which millions of micro-organisms, known as *symbiotic bacteria*, live (see Fig. 100). These bacteria, also known as *nitrogen-fixing bacteria*, have the power of changing the nitrogen, in the air around the roots of the plants, into nitrogen compounds which help the growth of the plant. The bacteria are parasites and secure their food from the plant, but they in turn supply the plant with an abundance of food containing the much-needed element nitrogen. In addition to supplying the plants on which they live with nitrogen, these bacteria "fix" more nitrogen, which remains in the soil to serve as food for other plants. This process is known as *nitrogen fixation* and it is often used in agriculture. A good farmer uses a system of crop rotation, in which each part of his cultivated land is planted with some type of leguminous crop at least once every four years. By growing such plants and then plowing them under the ground, the farmer can enrich his soil with fixed nitrogen.

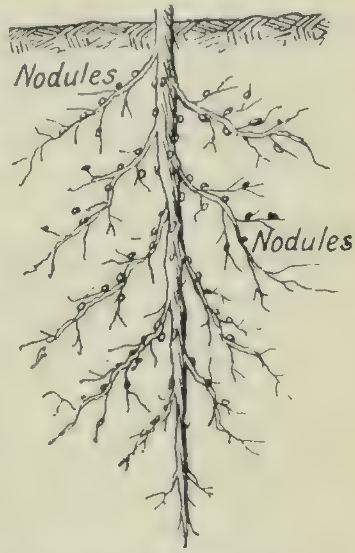


Fig. 100—Nodules on Root of Bean Plant

EXERCISES

1. (a) Why is nitrogen such an important element?
   (b) Can plants or animals take nitrogen directly from the air?

2. Would life such as we have it be possible, if
   (a) the atmosphere contained only nitrogen?
   (b) the nitrogen in the atmosphere were replaced by oxygen?
3. Where does nitrogen occur, (a) in the free state?
   (b) in the combined state?
4. How is phosphorus used in preparing nitrogen from the air? In this process, what becomes of the oxygen of the air? Illustrate your answer with a labelled diagram and write equations for the reactions involved.
5. How may pure nitrogen be obtained? Illustrate your answer with a labelled drawing and write the equations for the reactions which take place.
6. Write a short note on the preparation of nitrogen from the air for commercial use.
7. Why is there so much nitrogen in the air?
8. Give three physical properties which nitrogen has in common with hydrogen and oxygen.
9. If you were given five bottles filled with hydrogen, oxygen, carbon dioxide, carbon monoxide, and nitrogen respectively, how could you recognize each of them?
10. Name three elements with which nitrogen will combine directly.
11. Give two important uses of nitrogen in industry.
12. Plants such as clover, peas, beans and alfalfa have the power of taking nitrogen from the air and converting it into compounds of nitrogen.
    (a) What is this process called?
    (b) By what agencies is it brought about?
    (c) Of what value is this process to all of us?

Chapter XXV

THE ATMOSPHERE

1. Introduction

The term *atmosphere* is used in science to designate the mixture of gases which surrounds the earth. This mixture is also known as air but, as a rule, the latter term is used in referring to a small part of the atmosphere.

Torricelli, an Italian scientist, and a pupil of Galileo, first discovered that air has weight. This fact can be demonstrated in the laboratory by weighing a bottle of air, removing the air by means of a suction pump, and then weighing the bottle again. The decrease in weight gives the weight of the air removed from the bottle. Careful experiments have shown that *one litre of air at S.T.P. weighs 1.293 grams.*

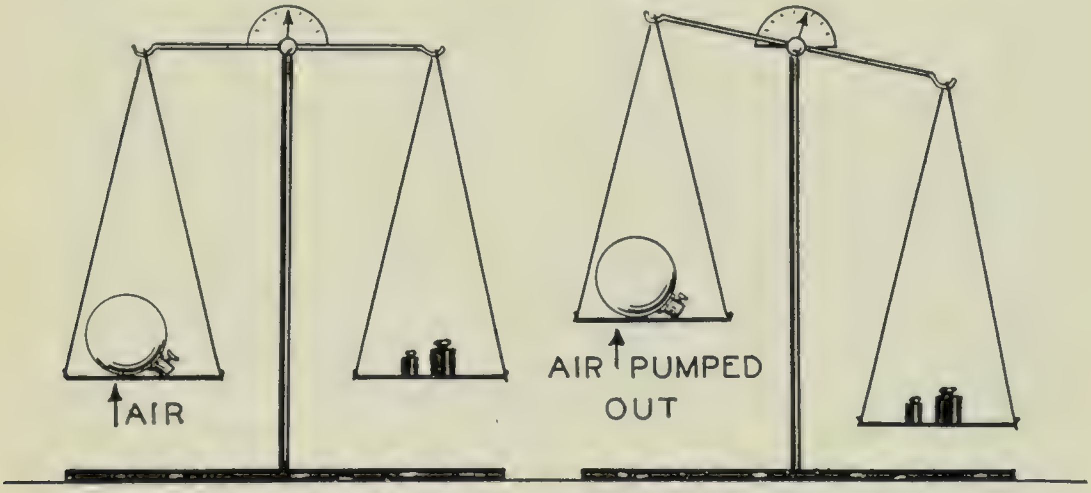


Fig. 101—An Experiment to Show that Air has Weight

This envelope of gas, extending to an unknown distance, which surrounds our planet, has been estimated to weigh about eleven and a half trillion pounds. It exerts a pressure of about fourteen tons on each person but, because this pressure is distributed evenly on all parts of the body, it does not cause inconvenience. At sea level, the average pressure of the atmosphere is 14.7 pounds per square inch, but the pressure is less on higher levels because the air above presses on that below, making the pressure greatest near the earth.

Air is necessary to both plant and animal life, and it is also vital to the process of burning. In addition to life and combustion, other phenomena which depend on the air are: the propagation of sound, the decay of plant and animal matter, twilight, solar and terrestrial radiation, and weather.

2. The Composition of the Atmosphere

It has already been found that the most important components of air are oxygen, nitrogen, water vapour and carbon dioxide. In addition to these four, there is only one other component the proportion of which exceeds 0.01 per cent. This is the element argon, which was discovered in the air by the British scientists, Lord Rayleigh and Sir William Ramsay, in 1894. The average composition of *dry* air is given in Table 12. These components, with the exception of water vapour, do not vary greatly in amount. The proportion of water vapour in the air varies very much with time and place, its maximum under ordinary conditions being about one per cent by weight and its minimum about 0.1 per cent.

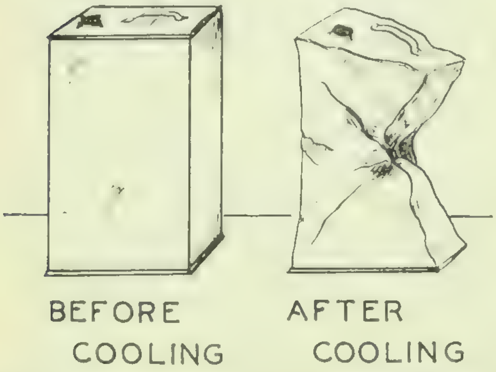
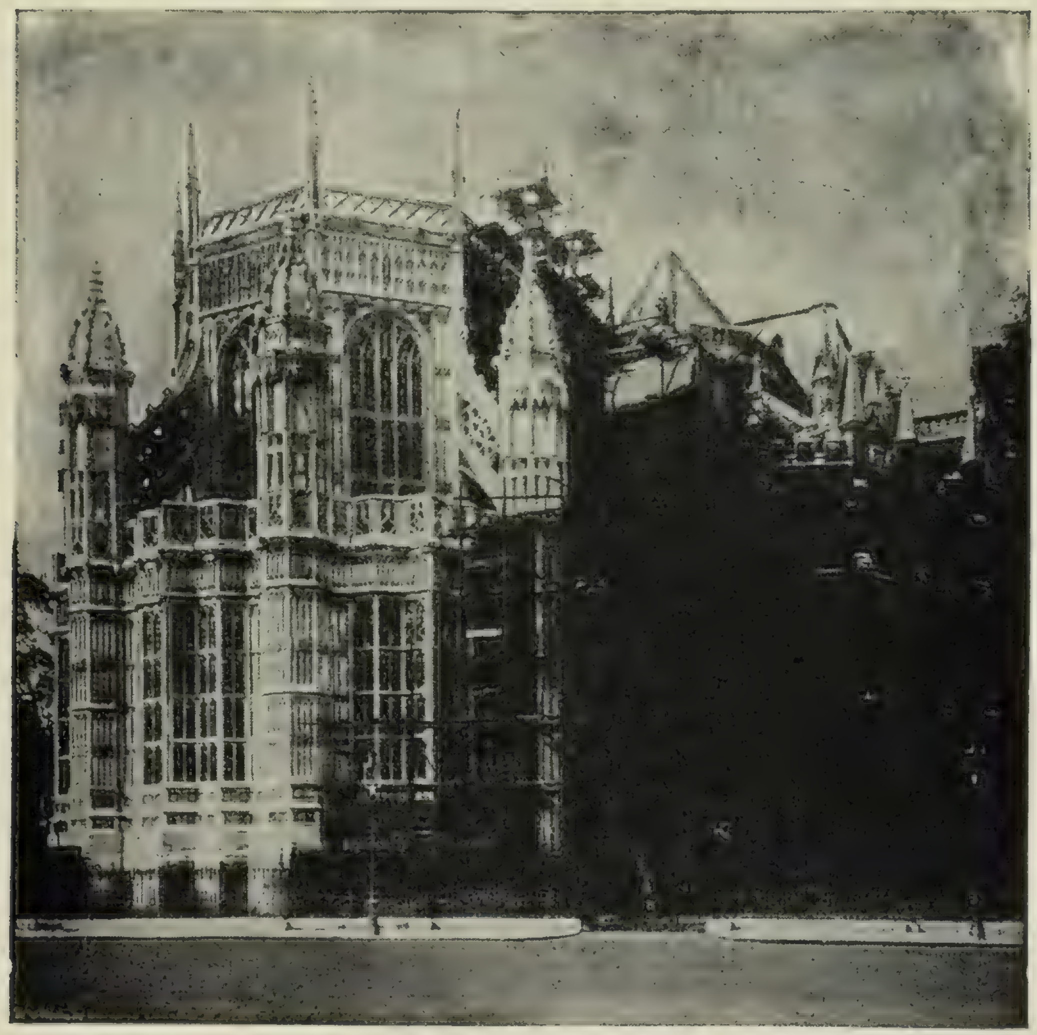


Fig. 102—An Experiment which Illustrates that the Atmosphere Exerts Pressure

In addition to the components shown in Table 12, there are also present in the air very small amounts of other substances. These include dust particles and certain micro-organisms, such as bacteria. In cities, much of the dust consists of small particles of carbon eliminated from chimneys as smoke. This represents an enormous loss of fuel. It also makes necessary extra washing of clothing, curtains and other things. Buildings must be cleaned occasionally as shown in Fig. 103. The air also contains very small amounts of several other gases, which are poured into it from manufacturing plants and by certain chemical changes which occur in nature. These gases are sometimes known as the *accidental components* of the air and they include hydrogen, methane, sulphur dioxide, hydrogen sulphide, ammonia, ozone, nitric oxide, and carbon monoxide. Most of these gases are active chemically; so, they are removed continuously from the air by various means. As a result of this, they are never present in the air in very large amounts.

TABLE 12—THE COMPOSITION OF DRY AIR

Components	By Volume	By Weight
Nitrogen	78.03%	75.46%
Oxygen	21.00%	23.20%
Argon	0.93%	1.30%
Carbon dioxide	0.04%	0.05%
Neon	1 part in 65,000	1 pound in 44 tons
Helium	1 part in 200,000	1 pound in 725 tons
Krypton	1 part in 1,000,000	1 pound in 173 tons
Xenon	1 part in 11,000,000	1 pound in 1208 tons
Water vapour	Variable within wide limits	



Courtesy of the British Commercial Gas Association

FIG. 103—HENRY VIII'S CHAPEL, WESTMINSTER ABBEY, WHILST BEING CLEANED

The cleaning process took several months. The part on the left cleaned first is already being coated again with soot, while the pinnacle on the right which has just been cleaned shows startingly white against the smoke-blackened building which has not been cleaned at all.

3. Air is a Mixture

Air is a mixture of gases, not a compound, because:

(1) The composition of the air is not definite. The percentages of some of its components show considerable variations. The percentage of oxygen is slightly greater in the country than in cities. The above fact gives definite proof that air is not a chemical compound, which according to the Law of Definite Proportions always has the same percentage composition.

(2) When oxygen and nitrogen are mixed together in the proportions in which they exist in air, there is no evidence of a chemical change. Energy, such as heat or light, is not given off, and this is a real test of a chemical combination. In addition, the gaseous mixture possesses all the properties of pure air. These facts prove that a compound is not formed when these elements come together under the conditions which exist in the atmosphere.

(3) When a pure compound dissolves in water, it does so as a whole. When air is mixed with water, a greater amount of oxygen than of nitrogen is dissolved. This would not be the case if the oxygen was combined with the nitrogen in a compound.

(4) Liquid air does not behave as a compound. A pure liquid has a definite boiling point, but when liquid air boils the more volatile nitrogen comes off first, leaving most of the oxygen behind. This is further proof that air is a mixture and not a compound.

4. Why the Composition of the Atmosphere Remains Constant

Because of certain changes which balance one another, the proportions of the various components of the air are nearly constant. It is clear that oxygen is removed from the air on every hand by the burning of fuels and by the respiration of all animals. If oxygen were not being continuously added to the atmosphere the percentage of this component would in time steadily decrease. It has been shown by scientists that all growing plants take in carbon dioxide from the air and water from the soil, from which they produce, in addition to other products, starch and oxygen, according to the following equation:

$$6\,CO_2 + 5\,H_2O \longrightarrow \underset{\text{starch}}{C_6H_{10}O_5} + 6\,O_2 \uparrow$$

The oxygen supplied to the air in this way serves to keep the percentage of this element fairly constant.

Closely associated with the oxygen balance in the air is that of carbon dioxide. The removal of this gas by growing plants is made up for by its formation in the burning of wood, coal, fuel gases, and other carbon compounds. Carbon dioxide is also thrown into the air in the respiratory process of animals and by the decay of all organic matter. Thus, the biological processes of plants balance the effects of animal respiration, combustion, and decay upon the composition of the atmosphere.

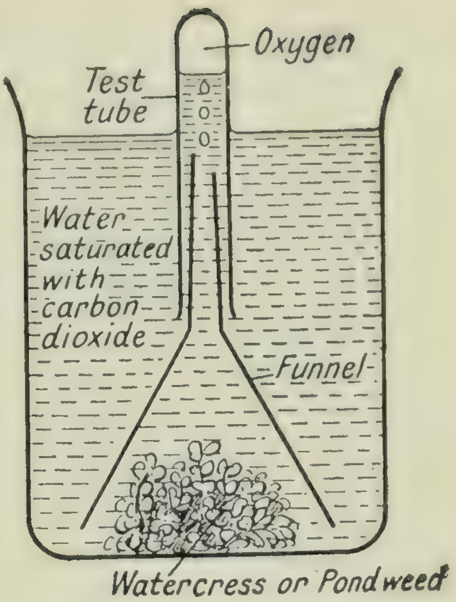


FIG. 104—OXYGEN PRODUCED BY PLANTS

The atmosphere as a whole is, of course, enormous in quantity, and the changes in composition due to various local causes are very quickly re-adjusted by diffusion, aided by wind.

5. Functions of the Components of the Atmosphere

(1) OXYGEN. Oxygen is necessary for the respiration of all plants and animals. Without this important component of the air all life, as we know it, would cease. Another important function of oxygen is that it supports the combustion of all fuels.

(2) NITROGEN. This gas is chemically inert and one of its chief functions is to dilute the oxygen of the air. If the air were composed entirely of oxygen, steel structures such as skyscrapers could be destroyed by fire. The presence of nitrogen in the air also moderates the process of respiration. Another important function of nitrogen is to supply the soil with nitrogen compounds. This was discussed in the last chapter under the heading of nitrogen fixation by plants (see page 185).

(3) CARBON DIOXIDE. The carbon dioxide in the air is an essential food of plants. Animals secure their nourishment from plants and man, in turn, obtains his food chiefly from plants and animals.

(4) WATER VAPOUR. The presence of water vapour in the air prevents the too rapid evaporation of moisture from plants and animals. Water vapour, on condensation, forms rain, without which most vegetation would perish, and there would be no streams.

The amount of moisture in the atmosphere is usually expressed in terms of *relative humidity*, the standard being the quantity needed to *saturate* the air at the existing temperature. The standard humidity is usually said to be 100 per cent and the average humidity of the atmosphere may be placed at about 66 per cent. Proper humidity is essential to good health. If the air is too dry in our homes, the skin becomes dry and cracks. It is also believed that dry air tends to bring on throat, nose, and lung diseases. Very dry air also causes furniture and walls to crack. It has been found that, in order to enjoy the greatest amount of comfort, the air of buildings should have a relative humidity of 35 to 50 per cent in winter, and 20 to 30 per cent in summer.

6. Liquid Air

When air is subjected to great pressures and much cooling, it is changed into a bluish coloured liquid, known as liquid air. The production of this material has already been described in the chapter on oxygen (see page 47).

Liquid air is a mixture, chiefly of liquid oxygen, boiling at $-183°$ C., and liquid nitrogen, boiling at $-196°$ C. This mixture boils at about $-190°$ C. and the more volatile nitrogen escapes first as a gas. Liquid air is an extremely cold substance; it readily changes such liquids as mercury and alcohol into solids. Tin, rubber, flowers, vegetables, and fruits become very brittle when immersed in liquid air. In fact most of these materials can be pulverized in a mortar after such treatment.

The manufacture of liquid air has become an important part of several industries which use oxygen, nitrogen, argon, and neon. It is also used to a considerable extent in scientific work, whenever very low temperatures are needed.

7. The Inert Gases

(1) HISTORICAL. In 1868, the English astronomer, Sir Norman Lockyer, detected a yellow line in the spectrum of the sun which was not reproduced in the spectrum of any of the substances then known on the earth. The name given to the new element was "helium," from the Greek word meaning "the sun."

In 1894, Lord Rayleigh observed that the density of nitrogen obtained from the air was always greater than that of nitrogen prepared from chemicals. Sir William Ramsay worked with Rayleigh and their researches led to the discovery of a new gas present in the atmosphere. This and other rare gases in atmospheric "nitrogen" caused it to weigh more than nitrogen produced chemically, which did not contain them. Much to the astonishment of the discoverers, the new gas did not undergo any kind of chemical change and so it was named "argon," from the Greek word meaning "inactive."

Shortly after the discovery of argon, Ramsay, in searching for other ways of producing the new element, examined the gas obtained by heating a mineral called clevite. At first it was thought that this gas was argon but an examination of its spectrum showed that, although argon was present, the gas was chiefly helium. In 1895, Kayser reported the presence of helium in the atmosphere, having detected its presence by means of the spectroscope.

Neon, krypton, and xenon were discovered by Ramsay and Travers, in 1898. The first of these was called "neon" from the Greek word meaning "new one." Krypton means "hidden one," and the last was named "xenon," or the "stranger."

(2) PROPERTIES. The inert gases are all colourless, odourless, and tasteless. They are non-inflammable and non-explosive. All are monatomic.

These gases are known as the inert gases because of their great chemical inactivity. While one or two compounds of certain inert gases are reported to have been prepared, such researches and the results obtained may be considered of scientific interest only. For all practical purposes these gases are to be considered non-reactive. Due to their comparative scarcity, they are also known as the "rare" gases.

With the exception of helium, the source of the rare gases commercially is the atmosphere. Table 12 gives the quantities of the gases contained in the atmosphere. The values for the chief components are quite accurate but the figures for the minor components should be considered only as being close to the true values. A study of Table 12 also shows that the quantities of the inert gases in the atmosphere are, indeed, very small and so justifies the use of the term "rare gases." For example, it has been calculated that to inhale the same volume of xenon from the atmosphere as one breath of air, a person would have to breathe for a period considerably longer than a year. It is important to realize that it is only because large factories are operating in industrial centres for the production of oxygen and nitrogen that the rare gases can be recovered from the air today at a cost which permits of their use in commerce.

(3) Uses of the Inert Gases. *Helium.* The chief use of helium is in lighter-than-air craft. Due to the fact that helium will not burn or explode and its lifting power is about 92 per cent that of hydrogen, it is an excellent gas for use in balloons.

Within recent years helium has been used in the production of artificial atmospheres which are supplied to divers and tunnel workers. Such operations are carried on under pressure and when compressed air is used the nitrogen present will dissolve in the blood stream. If a person, after working under such conditions, is allowed to reach the atmosphere at normal pressure within a short period of time, the nitrogen dissolved in the blood stream will be released in the form of bubbles, causing a condition known as the "bends." On the other hand, if these workers are supplied with an artificial atmosphere, which may be a mixture of 80 per cent helium and 20 per cent oxygen, it is found that the period of decompression is much more rapid and the worker can safely return to normal atmospheric conditions with much less danger. The reason for this is that helium is extremely insoluble.

Medical scientists have also studied the possible use of artificial atmospheres containing helium in the treatment of diseases where breathing is difficult. For example, in the case of asthma, a patient will secure great relief after a short period of time in an atmosphere of helium and oxygen. Since the density of such a mixture is less than the density of air, the patient can inhale a volume of the mixture large enough to give him his requirements of oxygen even though his air passages are partially blocked.

Scientists sometimes find use for helium in certain research work. For example, by evaporating liquid helium under reduced pressure, a temperature of −272.3° C., within 0.7° C. of absolute zero, has been reached.

Shortly after World War II, there was an increased industrial demand for helium because of the development of a satisfactory process for welding aluminum by helium-shielded arc welding.

Argon. The chief application of this gas is found in the incandescent lamp industry, which today uses tens of thousands of cubic feet per month. The hot tungsten filament in the bulb combines readily with most gases; so, being inert at all temperatures, argon is an excellent gas to place in the lamp. It is even more suitable for this purpose than nitrogen.

Neon. Neon and, sometimes, argon and helium are used in producing the tubes which are known as "neon signs." These tubes are used for outdoor advertising and in beacons for ships and airplanes. The colour of the light emitted by a "neon tube" depends upon the colour of the glass of which the tube is made and upon the nature of the gases inside the tube. Different colours are produced by different mixtures of argon, neon and mercury vapour in tubes made of glass of different colours.

Krypton and Xenon. Krypton and Xenon find some application in the field of gaseous tube lighting because it has been found that additions of very small quantities of these gases will bring about decided changes in the electrical characteristics of argon or neon. According to recent researches, it has been found that krypton and xenon may replace argon, the most plentiful of the rare gases, just as argon has replaced the more abundant nitrogen. It has been found that a 25-watt filament lamp containing krypton and xenon will operate at an efficiency one-third greater than the same lamp containing argon.

EXERCISES

1. (a) Describe an experiment which shows that air has weight.
   (b) What is the weight of one litre of air at S.T.P.?
   (c) What is the average pressure of the atmosphere at sea level?
2. (a) Tabulate the four most important components of the air.
   (b) Make a list of the other components of the air.
3. What facts prove that air is not a compound?
4. Explain carefully why the composition of the atmosphere is nearly constant.
5. Write a note on the functions of the components of the atmosphere.
6. Write a note on liquid air under: (1) Preparation, (2) Properties, (3) Uses.
7. (a) Make a list of the inert gases.
   (b) Tabulate the properties of these gases.
   (c) Why are they also known as the "rare" gases?
   (d) What is the commercial source of the rare gases?
   (e) Write a note on the uses of helium.
   (f) Tabulate the uses of argon, neon, krypton, and xenon.

Chapter XXVI

ACIDS, BASES AND SALTS

1. Acids

(1) Preparation. (a) *From the acid anhydride.* Oxides of non-metals are called acid anhydrides because they combine with water to form acids. The following examples illustrate this important method of preparing acids.

$$\underset{\text{carbon dioxide}}{CO_2} + H_2O \longrightarrow \underset{\text{carbonic acid}}{H_2CO_3}$$

$$\underset{\text{sulphur dioxide}}{SO_2} + H_2O \longrightarrow \underset{\text{sulphurous acid}}{H_2SO_3}$$

$$\underset{\text{sulphur trioxide}}{SO_3} + H_2O \longrightarrow \underset{\text{sulphuric acid}}{H_2SO_4}$$

$$\underset{\text{nitrogen pentoxide}}{N_2O_5} + H_2O \longrightarrow 2\ \underset{\text{nitric acid}}{HNO_3}$$

$$\underset{\text{phosphorus pentoxide}}{P_2O_5} + 3\ H_2O \longrightarrow 2\ \underset{\text{phosphoric acid}}{H_3PO_4}$$

Oxides of metals, on the other hand, are known as basic anhydrides because they combine with water to form bases. This difference in the behaviour of the oxides of metals and the oxides of non-metals towards water serves to distinguish *chemically* between metals and non-metals.

(b) *From a salt of the desired acid.* A good example of this method is the preparation of nitric acid by heating sodium nitrate with concentrated sulphuric acid.

$$2\ \underset{\text{sodium nitrate}}{NaNO_3} + \underset{\text{sulphuric acid}}{H_2SO_4} \longrightarrow \underset{\text{sodium sulphate}}{Na_2SO_4} + 2\ \underset{\text{nitric acid}}{HNO_3}\uparrow$$

Another good illustration of this method is the preparation of hydrochloric acid from common salt and concentrated sulphuric acid.

$$2\ NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ HCl \uparrow$$

(c) *From the elements.* Sometimes it is possible to prepare an acid from its elements by direct combination. For example, under the proper conditions, hydrogen will combine readily with chlorine to produce hydrogen chloride gas, which on being passed into water forms hydrochloric acid.

$$H_2 + Cl_2 \longrightarrow 2\ HCl$$

(2) PROPERTIES OF ACIDS. (a) *All contain hydrogen.* An examination of Table 13 shows that all acids contain the element hydrogen.

TABLE 13—SOME COMMON ACIDS

Formula	Name	Formula	Name
HCl	Hydrochloric Acid	$HC_2H_3O_2$	Acetic Acid
HNO_3	Nitric Acid	H_3PO_4	Phosphoric Acid
H_2SO_4	Sulphuric Acid	H_3PO_3	Phosphorous Acid
H_2CO_3	Carbonic Acid	HNO_2	Nitrous Acid
H_2SO_3	Sulphurous Acid	H_3BO_3	Boric Acid

(b) *Hydrogen replaceable by certain metals.* All metals above hydrogen in the electromotive series can replace hydrogen from dilute typical acids, such as sulphuric and hydrochloric. Zinc and iron are examples of metals which can readily replace hydrogen from dilute solutions of acids.

$$\underset{\text{Zinc}}{Zn} + \underset{\text{sulphuric acid}}{H_2SO_4} \longrightarrow \underset{\text{zinc sulphate}}{ZnSO_4} + \underset{\text{hydrogen}}{H_2\uparrow}$$

$$\underset{\text{iron}}{Fe} + \underset{\text{hydrochloric acid}}{2\ HCl} \longrightarrow \underset{\text{ferrous chloride}}{FeCl_2} + \underset{\text{hydrogen}}{H_2\uparrow}$$

The above type of chemical change is known as *simple replacement* or *simple displacement.*

Some substances contain hydrogen which cannot be replaced by metals; hence, such materials are not acids. For example, cane sugar, known by the chemist as sucrose, $C_{12}H_{22}O_{11}$, has plenty of hydrogen. However, it is not an acid because the hydrogen in its molecule is not replaced by metals. Ethyl alcohol, C_2H_5OH, benzene, C_6H_6, and hexane, C_6H_{14}, are other examples of compounds of this type. They are not classed as acids because the hydrogen in their molecules is not readily replaced by metals such as zinc or iron.

(c) *Water solutions of acids possess a sour taste.* Dilute solutions of all acids have a sour taste. The reason for this characteristic physical property of acids will be explained in the chapter on ionization.

(d) *Water solutions of acids always turn blue litmus paper red.* (The word *acid* and *red* both end in the letter *d* and this will help you to remember this fact.) This property of acids can be used as a simple test for acids and the reason for this phenomenon will be explained in the chapter on ionization.

(e) *All solutions of acids neutralize bases.* An important reaction to remember is as follows:

$$\text{Acid} + \text{Base} \longrightarrow \text{Salt} + \text{Water}$$

For example, the base, sodium hydroxide, neutralizes hydrochloric acid to produce common salt and water.

$$\underset{\substack{\text{hydrochloric}\\ \text{acid}}}{HCl} + \underset{\substack{\text{sodium}\\ \text{hydroxide}}}{NaOH} \longrightarrow \underset{\substack{\text{sodium}\\ \text{chloride}}}{NaCl} + \underset{\text{water}}{H_2O}$$

2. Bases

(1) PREPARATION. (a) *From the basic anhydride.* Oxides of metals are known as basic anhydrides because they combine with water to form bases. The following examples illustrate this important method of preparing bases.

$$\underset{\substack{\text{calcium}\\ \text{oxide}\\ \text{(quick-lime)}}}{CaO} + H_2O \longrightarrow \underset{\substack{\text{calcium}\\ \text{hydroxide}\\ \text{(Lime-water)}}}{Ca(OH)_2}$$

$$\underset{\substack{\text{magnesium}\\ \text{oxide}}}{MgO} + H_2O \longrightarrow \underset{\substack{\text{magnesium}\\ \text{hydroxide}}}{Mg(OH)_2}$$

(b) *From a salt of the desired base.* A good example of this method is the preparation of sodium hydroxide when sodium carbonate (a salt formed by the neutralization of sodium hydroxide by carbonic acid) reacts with calcium hydroxide.

$$\underset{\substack{\text{sodium}\\ \text{carbonate}}}{Na_2CO_3} + \underset{\substack{\text{calcium}\\ \text{hydroxide}}}{Ca(OH)_2} \longrightarrow \underset{\substack{\text{sodium}\\ \text{hydroxide}}}{2\,NaOH} + \underset{\substack{\text{calcium}\\ \text{carbonate}}}{CaCO_3\downarrow}$$

(c) *The action of water with certain gases.* For example, when ammonia gas is passed into water a base is produced which is known as ammonium hydroxide.

$$NH_3 + H_2O \longrightarrow NH_4OH$$

(2) PROPERTIES. (a) All bases contain the hydroxyl radical, OH.

(b) All bases in solution possess a peculiar biting, or caustic taste.

(c) All bases in solution have a soapy feeling.

(d) All bases in solution turn red litmus to blue. (The words *base* and *blue* both end in the letter *e* and this will help you to remember this fact.)

(e) Bases neutralize acids.

3. Neutralization

(1) DEFINITION. Neutralization is a process in which an acid in solution is added to a base in solution until the properties of both are destroyed.

(2) INDICATORS. In order to tell when an acid is neutralized by a base we must use certain complex chemicals, usually organic, which are known as indicators. Litmus, phenolphthalein, and methyl orange, are three indicators which are used a great deal in chemical laboratories.

(3) THE END-POINT. The end-point is the name given to that place in a neutralization experiment when a change in colour of the indicator tells us that the acid has been neutralized by the base. For example, when neutralizing an acid with a base, using methyl orange as the indicator, we stop adding the base to the acid when the indicator changes from a red colour to an orange. The neutralization of an acid by a base is a reaction which can be studied carefully by means of a method known as titration. Titration consists of allowing a measurable volume of one solution to flow from an instrument, called a burette, into a known volume of another solution until a certain reaction is complete.

(4) EXAMPLES. Many illustrations of neutralization could be selected but those given below are often encountered in the laboratory.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

$$2\ NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ H_2O$$

$$2\ NaOH + H_2CO_3 \longrightarrow Na_2CO_3 + 2\ H_2O$$

$$KOH + HNO_3 \longrightarrow KNO_3 + H_2O$$

$$Ca(OH)_2 + H_2CO_3 \longrightarrow CaCO_3\downarrow + 2\ H_2O$$

The above reactions are all examples of *double decomposition or metathetical reactions.*

4. Salts

(1) DEFINITION. A salt is a compound formed by replacing the replaceable hydrogen atoms in the molecule of an acid by a metal or a metallic radical.

(2) METHODS OF PREPARATION. (a) *Neutralization.* This

method is often used to prepare soluble salts. A good example is the neutralization of sodium hydroxide by hydrochloric acid.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

(b) *Metal and acid.* When dilute acids react with metals above hydrogen in the electromotive series, a salt of the acid used is produced and hydrogen is evolved as a gas. A good illustration is the action of dilute hydrochloric acid on zinc.

$$Zn + 2\ HCl \longrightarrow ZnCl_2 + H_2\uparrow$$

(c) *Acid and salt of a more volatile acid.* Hydrochloric acid, for example, is more volatile (evaporates more readily on warming) than sulphuric acid. Hence, when concentrated sulphuric acid is added to sodium chloride (a salt of hydrochloric acid), sodium sulphate and hydrochloric acid gas are produced.

$$2\ NaCl + H_2SO_4 \longrightarrow 2\ HCl\uparrow + Na_2SO_4$$

Another illustration is the action of concentrated sulphuric acid on sodium nitrate (Chile saltpetre).

$$2\ NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ HNO_3\uparrow$$

(d) *Metallic oxide and acid.* This method is often used in commerce for the preparation of salts. For example, sulphuric acid reacts with magnesium oxide to form magnesium sulphate.

$$MgO + H_2SO_4 \longrightarrow MgSO_4 + H_2O$$

(e) *Carbonate and acid.* Since certain carbonates are quite plentiful this method is often used in industry to prepare salts. For example, calcium carbonate (limestone) reacts with hydrochloric acid to form calcium chloride, carbon dioxide, and water.

$$CaCO_3 + 2\ HCl \longrightarrow CaCl_2 + H_2O + CO_2\uparrow$$

Another illustration is the reaction of sodium carbonate with dilute hydrochloric acid.

$$Na_2CO_3 + 2\ HCl \longrightarrow 2\ NaCl + H_2O + CO_2\uparrow$$

(f) *Direct combination.* Sometimes salts can be produced by the direct combination of their constituent elements. For example, when iron filings are heated with powdered sulphur, the salt, iron sulphide, is produced.

$$Fe + S \longrightarrow FeS$$

Another example is the action of chlorine on metallic sodium

$$2\ Na + Cl_2 \longrightarrow 2\ NaCl$$

(g) *By precipitation.* Insoluble salts are often prepared by precipitation. Thus, when a solution of hydrochloric acid is added to a solution of lead nitrate, a precipitate of lead chloride is produced.

$$2\ HCl + Pb(NO_3)_2 \longrightarrow PbCl_2\downarrow + 2\ HNO_3$$

Again, when silver nitrate solution is added to sodium chloride solution, a precipitate of silver chloride is formed.

$$AgNO_3 + NaCl \longrightarrow AgCl\downarrow + NaNO_3$$

Lead chloride and silver chloride are examples of insoluble salts.

(h) *Acid anhydride and basic anhydride.* When calcium oxide, commonly known as quicklime, is exposed to the air it slowly combines with the carbon dioxide of the air to form the salt, calcium carbonate.

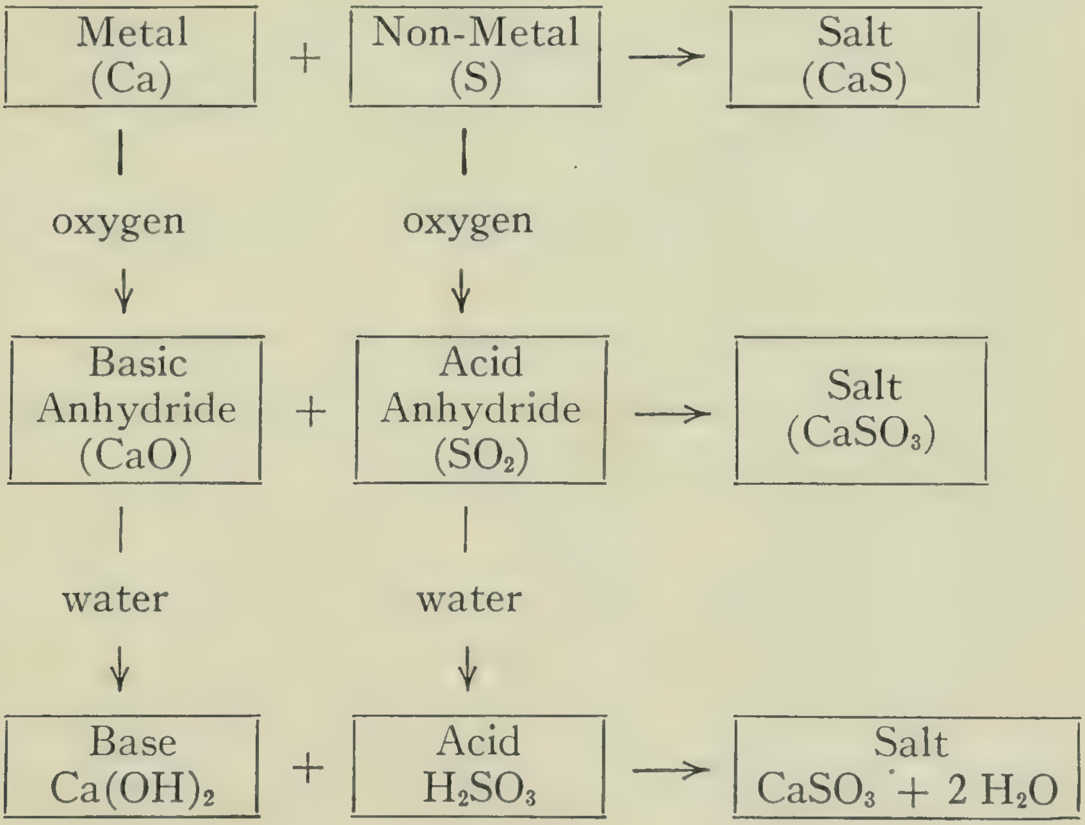
$$\underset{\substack{\text{calcium}\\ \text{oxide}}}{CaO} + \underset{\substack{\text{carbon}\\ \text{dioxide}}}{CO_2} \longrightarrow \underset{\substack{\text{calcium}\\ \text{carbonate}}}{CaCO_3}$$

Another example is the action of sulphur trioxide with magnesium oxide.

$$\underset{\substack{\text{magnesium}\\ \text{oxide}}}{MgO} + \underset{\substack{\text{sulphur}\\ \text{trioxide}}}{SO_3} \longrightarrow \underset{\substack{\text{magnesium}\\ \text{sulphate}}}{MgSO_4}$$

Many important applications of this reaction between an acid anhydride and a basic anhydride are found in chemical industries.

A few of the more important relationships considered in this chapter are reviewed in the following diagram.



EXERCISES

1. (a) What is the outstanding chemical difference between metals and non-metals?
   (b) Define basic and acid anhydrides.
2. (a) Tabulate three methods of preparing acids. Give one equation for each method.
   (b) Tabulate five properties of acids.
3. (a) How are bases prepared? Illustrate with equations.
   (b) Tabulate five properties of bases.
4. (a) What is neutralization? Give three examples.
   (b) What are indicators? Name three.
   (c) What is meant by the term end-point?
   (d) What is the process of titration?
5. (a) What is a salt? How does a salt differ from an acid or a base?
   (b) Tabulate six methods of preparing salts. Give one equation for each method.

CHAPTER XXVII

CHEMICAL NOMENCLATURE

1. Bases

Chemists have devised a system of naming chemical compounds. This is known as chemical nomenclature and it is important for the student of chemistry to master this systematic naming of compounds. The chief compounds encountered in elementary chemistry are acids, bases, and salts; so, the naming of these will be considered carefully.

All bases contain the hydroxyl group (OH) and this fact is indicated by the word hydroxide. Thus, NaOH is called sodium hydroxide, KOH is potassium hydroxide, $Mg(OH)_2$ is magnesium hydroxide, $Ca(OH)_2$ is calcium hydroxide, and NH_4OH is ammonium hydroxide. The rule for the naming of bases is apparent from the above examples. It is to prefix the *name of the metal or the metallic radical to the word hydroxide.*

2. Acids

(1) BINARY ACIDS. The acids usually encountered in elementary chemistry can be classified into two groups: binary and ternary. *A binary compound contains only two elements. A ternary compound*, on the other hand, *contains three different elements.* Thus, hydrochloric acid, HCl, is a binary acid, whereas sulphuric acid, H_2SO_4, is a ternary acid. An examination of Table 14 reveals the rule for the naming of binary acids. It is to use the *prefix "hydro" with the name of the other element in the acid and it always has the ending "ic."*

TABLE 14—SOME BINARY ACIDS AND THEIR SODIUM SALTS

Formula of Acid	Name of Acid	Formula of Salt	Name of Salt
HF	Hydrofluoric	NaF	Sodium fluoride
HCl	Hydrochloric	NaCl	Sodium chloride
HBr	Hydrobromic	NaBr	Sodium bromide
HI	Hydriodic	NaI	Sodium iodide
H_2S	Hydrosulphuric	Na_2S	Sodium sulphide

(2) TERNARY ACIDS. Most of these acids contain oxygen as the third element; so, they are often called *oxygen acids* or

oxy-acids. These acids are grouped into families and a study of Table 15 shows how they are named. It is important to memorize the formulas and names of these groups of acids because this information is necessary in order to be able to write the formulas and names of the salts derived from these acids.

If there is a series of these acids, as in the case of the chlorine oxy-acids (see Table 15), the best-known one is named after the characteristic element (without its termination) with the suffix—*ic;* e.g., chlor*ic* acid, $HClO_3$. $HClO_4$, containing one more atom of oxygen in its molecule than chloric acid, is known as *per*chloric acid. $HClO_2$, having one less atom of oxygen in its molecule than chloric acid, is called chlor*ous* acid. Finally, $HClO$, with the least number of oxygen atoms in its molecule, is known as *hypo*chlor*ous* acid. Some families of acids are not as complete as the chloric acid group because some of their members cannot be prepared in the laboratory.

TABLE 15

SOME IMPORTANT TERNARY ACIDS AND THEIR SODIUM SALTS

Formula of Acid	Name of Acid	Formula of Salt	Name of Salt
$HClO_4$	*Per*chlor*ic*	$NaClO_4$	Sodium *per*chlor*ate*
$HClO_3$	Chlor*ic*	$NaClO_3$	Sodium chlor*ate*
$HClO_2$	Chlor*ous*	$NaClO_2$	Sodium chlor*ite*
$HClO$	*Hypo*chlor*ous*	$NaClO$	Sodium *hypo*chlor*ite*
H_2SO_4	Sulphur*ic*	Na_2SO_4	Sodium Sulph*ate*
H_2SO_3	Sulphur*ous*	Na_2SO_3	Sodium sulph*ite*
HNO_3	Nitr*ic*	$NaNO_3$	Sodium nitr*ate*
HNO_2	Nitr*ous*	$NaNO_2$	Sodium nitr*ite*
H_2CO_3	Carbon*ic*	Na_2CO_3	Sodium carbon*ate*
H_2CO_2	Carbon*ous*	Na_2CO_2	Sodium carbon*ite*
H_3PO_4	Phosphor*ic*	Na_3PO_4	Sodium phosph*ate*
H_3PO_3	Phosphor*ous*	Na_3PO_3	Sodium phosph*ite*

3. Salts

(1) BINARY. The name of a salt depends upon the acid from which it is derived. A study of Table 14 shows that all binary salts end in "*ide*" and they include the name of the metal

as well as a contraction of the other constituent. Thus, $NaCl$, a salt of hydrochloric acid, is called sodium chloride. $NaBr$, a salt of hydrobromic acid, is known as sodium bromide. Na_2S, a salt of hydrosulphuric acid, is called sodium sulphide.

(2) TERNARY. An examination of Table 15 reveals the system of naming ternary salts. The prefixes are carried through from the name of the acid into the name of the salt. Thus, $NaClO_4$, a salt of perchloric acid, is called sodium perchlorate. It should be observed that the "*ic*" ending of the ternary acid always changes to "*ate*" in the name of the salt. The "*ous*" ending of the ternary acid changes to "*ite*" in the name of the salt. Thus, Na_2SO_3, a salt of sulphurous acid, is known as sodium sulphite.

4. Radicals

(1) DEFINITION. A radical consists of a group of different atoms, combined together into a single unit, which goes through most chemical reactions unchanged.

(2) EXAMPLES. The hydroxyl radical, OH, found in all bases, is a good example of a radical. The sulphate radical, SO_4, present in sulphuric acid and in all sulphates, is another good illustration of a radical.

(3) PROPERTIES. Radicals are not found in the free state; so, they are always associated with some other radical or atom. A few years ago certain organic radicals were isolated in the free state for a fraction of a second. This is of great scientific interest, but radicals are so reactive that they combine as soon as they are produced with some atom or some other radical. A radical has a definite valence and the valences of some common radicals are given in Table 16. Most of the radicals encountered in elementary chemistry are known as acid radicals because

TABLE 16—THE VALENCES OF SOME COMMON RADICALS

Formula of Radical	Name	Valence	Formula of Radical	Name	Valence
NH_4	Ammonium	+ 1	SO_3	Sulphite	− 2
OH	Hydroxyl	− 1	SO_4	Sulphate	− 2
NO_2	Nitrite	− 1	PO_3	Phosphite	− 3
NO_3	Nitrate	− 1	PO_4	Phosphate	− 3
ClO_3	Chlorate	− 1	SiO_3	Silicate	− 2
ClO_2	Chlorite	− 1	$C_2H_3O_2$	Acetate	− 1
ClO	Hypochlorite	− 1	CO_3	Carbonate	− 2

they are found joined with hydrogen to produce acids. They have a negative valence.

5. Naming of Other Compounds

It is important to remember that, although acids, bases, and salts are encountered a great deal in elementary chemistry, there are, however, many other different types of compounds. For example, there are about 300,000 carbon compounds and the organic chemist has developed a system of naming these compounds. The names of a few organic compounds will be considered in the chapters on organic chemistry. Carbides, oxides, hydrides, and nitrides are important classes of compounds. A typical carbide is calcium carbide, CaC_2, which is used in the preparation of acetylene gas. Calcium oxide, CaO, known commercially as quicklime, is an excellent example of an oxide. Nitrogen hydride, NH_3, commonly known as ammonia, is an illustration of a hydride. Magnesium nitride, Mg_3N_2, is a typical nitride. It is produced along with magnesium oxide, MgO, when magnesium ribbon is burned in air.

EXERCISES

1. (a) What is meant by chemical nomenclature?
   (b) How are bases named? Give three examples.
2. (a) Define the terms binary and ternary.
   (b) What is the rule for naming binary acids?
   (c) Write the names and formulas of three binary acids.
3. (a) What is a ternary acid?
   (b) Write out the formulas and names of the members of the chloric acid family.
4. (a) How are salts named? Give three examples of binary salts and five examples of ternary salts.
   (b) What is a radical? Are radicals found in the free state?
   (c) Write the formulas for the following radicals and state the valence of each: sulphate, phosphate, ammonium, carbonate, chlorite, nitrate, and sulphite.
5. Name the following compounds: CaC_2; Fe_2O_3; NH_3; HI; $HClO_4$; H_3PO_4; H_2CO_3; KOH; CaO; KNO_3; $ZnSO_4$; $SnCl_4$; $NaNO_2$; NH_4Cl; $CaCl_2$; Na_2CO_3; Mg_3N_2; FeS; $CaCO_3$; Na_2SO_3.

CHAPTER XXVIII

THE MODERN THEORY OF THE ATOM

1. Introduction

Many years ago John Dalton, an English schoolmaster, gave to science a very important theory concerning the structure of matter. This theory, known as Dalton's atomic theory, assumes that every chemical element, such as oxygen, iron, or gold, is made up of very small indivisible particles called atoms. Dalton believed that the atoms of different chemical elements have different weights, but that those of a particular element are alike and constant in weight. According to his theory chemical compounds, such as common salt and water, are formed by the chemical union of the atoms of different elements. For example, an atom of sodium combines with an atom of chlorine to form a molecule of salt, sodium chloride, while two atoms of hydrogen combine with one atom of oxygen to form a molecule of water.

Recent studies of the properties of matter forced scientists to assume the existence of particles still smaller than atoms; so Dalton's idea of the atom has been changed somewhat. The modern chemist believes that the atom has a very complex structure, and that it is composed of small particles distributed within the space that it occupies somewhat like the arrangement of the sun and the planets of the solar system. Dalton thought of the atom as a hard, solid particle, but the modern view is that the atom is porous. The several kinds of particles which make up the atom occupy only a small portion of the whole space occupied by the atom. The three chief kinds of particles which compose atoms are *electrons*, *protons*, and *neutrons*.

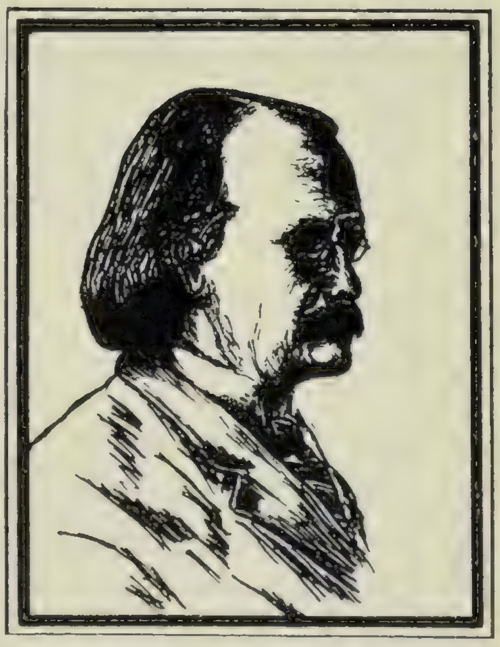


FIG. 105—SIR J. J. THOMSON, DISCOVERER OF THE ELECTRON

2. Electrons

In 1897 Sir Joseph Thomson, a great English scientist, showed that atoms contained very small electrically charged particles known as electrons. The chief facts about an electron are as follows:

(1) It carries a unit *negative* charge of electricity. There is no electric charge smaller than that on the electron, and so the charge on the electron is a fundamental unit of electricity. All other charges are multiples of its charge.

(2) The mass of an electron is $\frac{1}{1845}$ that of the hydrogen atom.

(3) The electron is a constituent of all atoms.

3. Protons

Scientists searched for a *positively* charged particle corresponding to the electron in mass and charge. This problem was solved by the outstanding British physicist, Lord Rutherford, who discovered the proton. The chief facts about a proton are as follows:

(1) It is a *positively* charged particle carrying the same amount of electricity as an electron, but it has the opposite sign (+ instead of −).

(2) The mass of a proton is almost the same as the mass of an atom of hydrogen, 1.008 as compared with 16 for the mass of an atom of oxygen.

FIG. 106—LORD RUTHERFORD, DISCOVERER OF THE PROTON

Some years ago he was a professor of physics at McGill University, Montreal.

4. Neutrons

In 1932 Sir James Chadwick, in England, discovered the neutron, an electrically neutral particle, by bombarding the element beryllium with alpha particles (He^{++}). The chief facts about a neutron are:

(1) It has no electrical charge.

(2) Its mass is approximately 1.008 as compared with 16 for the oxygen atom.

At first the neutron was considered to be composed of one proton combined with one electron. Now, however, it is regarded as a distinct kind of particle. The reason that scientists believe that neutrons are a part of the structure of atoms is that these particles can be expelled from many kinds of atoms by bombardment.

5. The Structure of an Atom

All the protons and neutrons of any atom are found in a compact central region called the nucleus. All atomic nuclei contain both kinds of particles, with the exception of the hydrogen nucleus which is a single proton. The nucleus, therefore, is always positively charged. Enough electrons to balance the number of protons in the nucleus make up the remainder of the atom's structure. This must be true, because the atom, as a whole, is electrically neutral. The electrons are located in the outer part of the atom and scientists believe that they revolve around the nucleus in orbits of various sizes and forms, some circular and some elliptical. This picture of the atom resembles the solar system. The nucleus corresponds to the sun and the outer electrons to the planets.

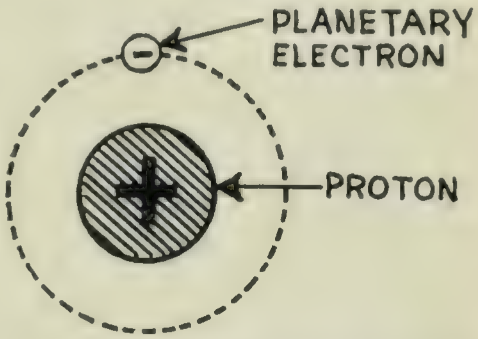


Fig. 107—The Hydrogen Atom (Simplest), Showing a Proton in the Centre and the Single Planetary Electron Rotating in Its Orbit

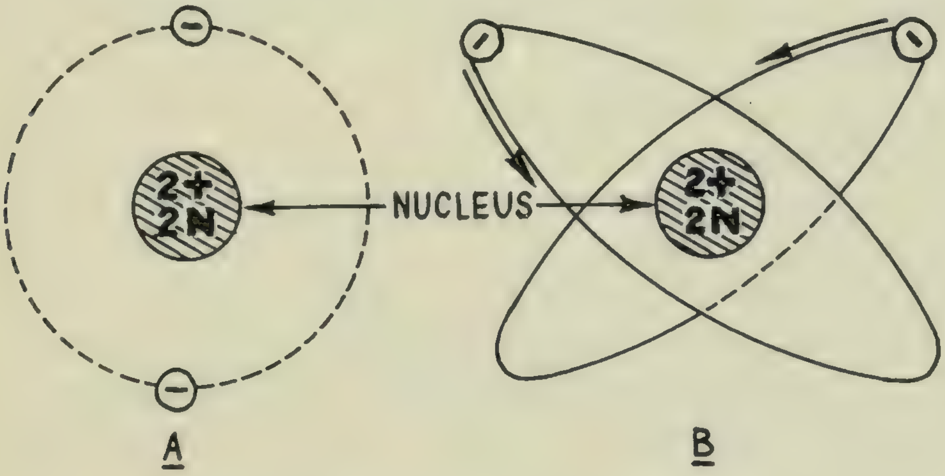


Fig. 108—Structure of Helium

A represents the electrons revolving in circular orbits. B represents the Bohr idea, where each electron occupies its own orbit.

There are 92 elements and so there are 92 kinds of atoms. Hydrogen atoms, consisting of only one proton and one electron, are the lightest. Uranium atoms are nearly the heaviest, having 238 protons and neutrons, and 92 electrons. In all atoms, the electrons are alike and interchangeable, like standardized bricks used in all sorts of buildings.

Under normal conditions the diameter of a hydrogen atom is estimated to be about a hundred millionth of a centimetre (2.54 centimetres equal 1 inch), which appears to be about twice the usual distance of its electron from its nucleus. The size of an electron is not known with accuracy but it is a very small fraction of the size of the whole atom. The nucleus, or central sun, appears also to be extremely small as compared to the size of the entire atom. From the above it is apparent that an atom is largely a vacuum. It has been calculated that if the nucleus of a helium atom were represented by a pea, its two planetary electrons could be represented by two peas a quarter of a mile away. The electron of the hydrogen atom travels around its tiny orbit at a tremendous speed, thousands of miles per second. It is this rapid revolving of the electrons in an atom which keeps everything out of the space within quite as effectively as though they were everywhere at once. The only things which can get inside an atom are smaller things, fragments of other atoms, protons, neutrons, or electrons. They must be shot at their targets at just the right speed.

The information concerning the structure of atoms has been obtained by means of the spectroscope, by X-rays, and from a study of such elements as radium, which are continually breaking down into other elements.

Some of the chief facts about the structure of the atom are summarized below:

(1) The atom is composed of three chief types of particles: protons, neutrons, and electrons.

(2) The atom is electrically neutral. This is because the amount of electricity on a proton is equal to the amount on an electron, and the number of electrons in an atom always equals the number of protons.

(3) All the protons and neutrons are closely packed and make up the nucleus of the atom. In the lighter atoms the number of protons usually equals the number of neutrons, but in the heavier atoms the number of neutrons exceeds the number of protons.

(4) The nucleus, due to the presence of protons, is positively charged.

(5) Around the nucleus and at relatively great distances from it are the electrons. They are known as *planetary* or *satellite* electrons.
(6) It is the number of planetary electrons in the outermost layer which determines the chemical properties of an element.

6. Atomic Numbers

In 1914 Henry Moseley, a brilliant young English chemist, discovered a very important relationship among the elements which has been of great value in the study of atomic structure. He studied the X-ray spectra of various elements and found a definite change in wave lengths as he went from the lighter to the heavier elements. As a result of his research, all the elements can be given a serial number. For example, the serial number for hydrogen is one, for carbon is 6, for oxygen is 8, and for uranium is 92. These numbers are known as *atomic numbers* and they are the same as the *number of protons or planetary electrons* present in the atoms under consideration. Moseley arranged all the elements in a series according to their atomic numbers. The series starts with hydrogen, with one electron outside the nucleus, and ends with uranium, which has 92 planetary electrons. Each element differs from its neighbour by one electron. In the case of the lighter elements, the atomic number is usually one-half the atomic weight. For example, the atomic number of oxygen is 8, which is one-half of its atomic weight.

7. Electron Orbits

Chemists know that the number of electrons in an atom is the same as the number of protons. It is also known that the electrons are outside the nucleus and undoubtedly they are in motion. However, scientists are not sure about the exact position and motion of the electrons. Experiments seem to show that they revolve in orbits about the nucleus. The orbit nearest the nucleus can hold only 2 electrons. The second and third orbits hold a maximum of 8 each, and succeeding orbits can hold increasingly greater numbers. Sometimes it is said that the electrons revolve in *imaginary concentric shells* about the nucleus rather than in orbits. It does not make much difference which of these terms is used and so the idea of *orbit* will be used, since it is simpler to represent the electrons in diagrams as revolving in orbits.

The diagrams for the first eleven elements in the ascending order of their atomic numbers are shown in Fig. 109. The nucleus is represented by a small inner circle, the electrons by a small circle with a minus sign inside it ⊖, and the orbits in which the electrons revolve by circles surrounding the nucleus.

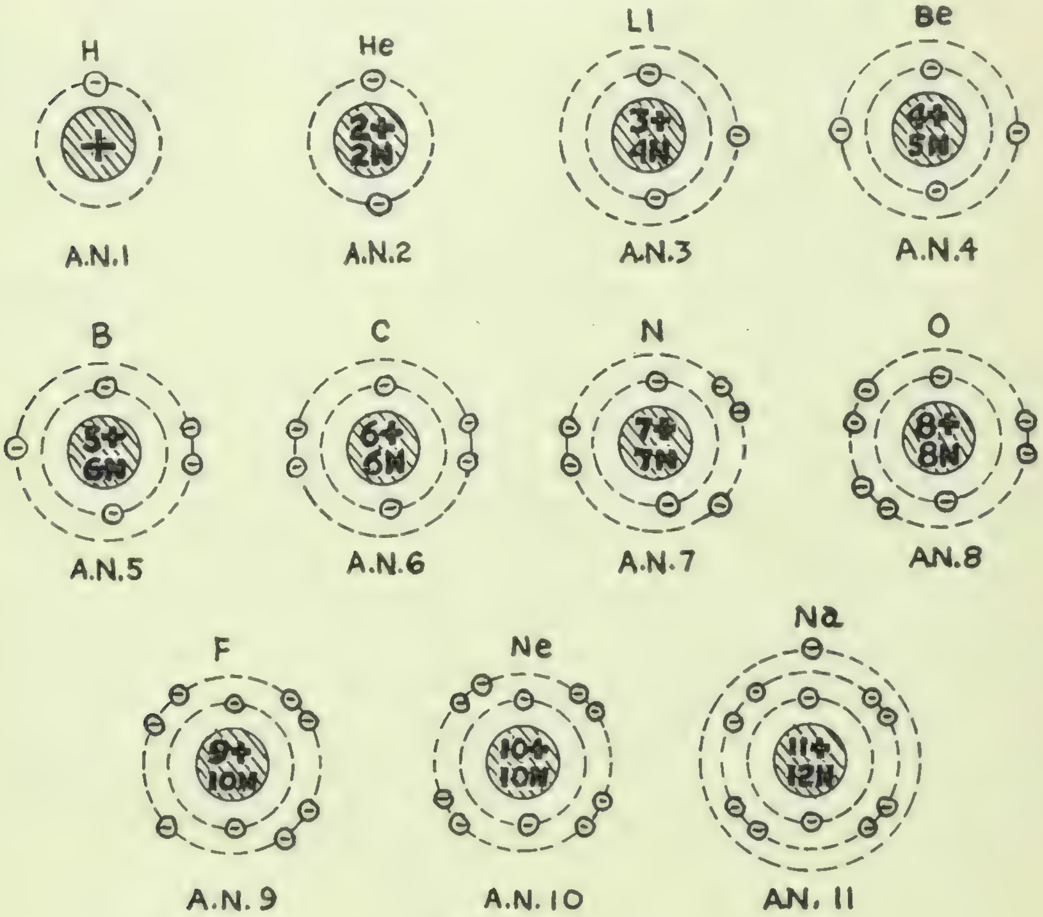


Fig. 109

The electronic structure of atoms from hydrogen to sodium inclusive. A.N. represents the atomic number. (The letter N in the nucleus represents a neutron.)

Inside the nucleus are shown the numbers of protons (+) and neutrons (N) and the atomic weight is due to the total number of these particles present in its nucleus. Underneath each diagram is shown the atomic number (A.N.). A careful examination of these diagrams shows that:

(1) *Hydrogen*, the smallest of all atoms, has a nucleus of one proton around which revolves one electron. It is the only atom which has no neutrons in the nucleus. Its atomic number is one.

(2) *Helium* has a nucleus consisting of 2 neutrons and 2 protons and so its atomic weight is 4. It has 2 planetary electrons, both in the same orbit, relatively close to the nucleus. The atomic number of helium is 2.

(3) *Lithium* has 3 protons and 4 neutrons in its nucleus making its atomic weight 7. It has 3 planetary electrons. Two of these, as in the case of helium, are in the first orbit close to the nucleus. The third electron is in a new orbit some distance away. The atomic number of lithium is 3. It is observed that beryllium has 2 electrons in its second orbit, boron has 3, carbon 4, nitrogen 5, oxygen 6, and fluorine 7.

(4) *Neon* has 10 protons and 10 neutrons in its nucleus and so its atomic weight is 20. There are 2 electrons in the first orbit and 8 in the second. The atomic number of neon is 10.

(5) *Sodium* has 11 protons and 12 neutrons in its nucleus. The first orbit contains 2 electrons, the second has 8 and the third one. The atomic number of sodium is 11.

8. Electrons and Chemical Activity

In the study of electron orbits it was found in the case of the lighter atoms that the first orbit is completely filled with 2 electrons, the second with 8, and the third with 8. This fact is so important that a special name is given to the *outside orbit* (of 8 electrons when completed), namely, the *octet* of the atom.

Research has shown that those atoms which have completed octets, with rare exceptions, never combine with other atoms nor with each other. They have no chemical affinity for any substance and so they possess no valence. They are the atoms of the inert gases, namely: helium, neon, krypton, xenon and radon. The numbers of electrons in the various orbits of these atoms are shown in Table 17.

TABLE 17—THE ARRANGEMENT OF THE ELECTRONS IN THE ATOMS OF THE INERT GASES

Name of Element	Symbol	Orbit 1	Orbit 2	Orbit 3	Orbit 4	Orbit 5	Orbit 6
Helium	He	2	..	..	..	..	..
Neon	Ne	2	8	..	..	..	..
Argon	A	2	8	8	..	..	..
Krypton	Kr	2	8	18	8	..	..
Xenon	Xe	2	8	18	18	8	..
Radon	Rn	2	8	18	32	18	8

All atoms, on the other hand, *with incomplete octets have chemical affinity and valence.* This fact gives us the clue to the secret of chemical affinity and valence. Chemical activity depends upon the number of electrons in the outermost orbit. If the outer ring is complete, the element is inert. If the outermost orbit lends one electron or borrows one, the element is very active. If the outer ring lends or borrows 2, the element is fairly active; if 3, the element is not very active. For example, fluorine and chlorine are very active elements because their atoms have 7 electrons in their outermost orbits. These atoms have a marked tendency to pick up one electron to complete their octet. Some metallic elements, such as sodium and potassium, are very active because their atoms have only one electron in the outermost orbit. These atoms have a strong tendency to lose one electron so that the outermost orbit will have a completed octet.

There are two chief ways in which completed octets may be formed. These are:

(1) By the gain or loss of electrons.
(2) By sharing electrons.

9. Gain or Loss or Electrons

A good illustration of this type of chemical action is the formation of common salt, sodium chloride, from its constituent elements. This reaction was explained in the days of John Dalton by saying that atoms of the element sodium have a great *chemical affinity* for the atoms of the element chlorine. These two atoms, therefore, combine together very readily to form molecules of sodium chloride. Since the affinity of these two atoms for each other is so great, the resulting molecule, NaCl, is an extremely stable one. This reaction can be expressed as follows:

$$\mathbf{Na + Cl \longrightarrow NaCl}$$

The modern chemist, because of his increased knowledge concerning the structure of the atom, explains the combination of sodium with chlorine in a more complicated way. The sodium atom with one electron in its outer orbit will lose this electron to a chlorine atom. When this takes place both the sodium and chlorine atoms have complete outer orbits of 8 electrons as shown in Fig. 110. Before giving up the one electron in its outer orbit to the chlorine atom, the sodium atom was electrically neutral. Now, however, it is positively charged because it has one more proton (+) in its atom than electrons ⊖. The chlorine atom was also electrically neutral at the start, but since it gained one electron from the sodium atom it now has a negative charge. It has one more electron $\ominus$ in its atom than protons $(+)$. These electrically charged atoms (Na^+ and Cl^-) are known as ions and they are held together in chemical combination by their opposite electrical charges.

Atoms which lose one electron to form positively charged ions have a valence of one; atoms which lose 2 electrons have a valence of 2; those which lose 3 have a valence of 3 and so forth. Atoms which gain one electron to produce negatively charged ions have a valence of one; atoms which gain 2 electrons have a valence of 2; those which gain 3 have a valence of 3, and so forth.

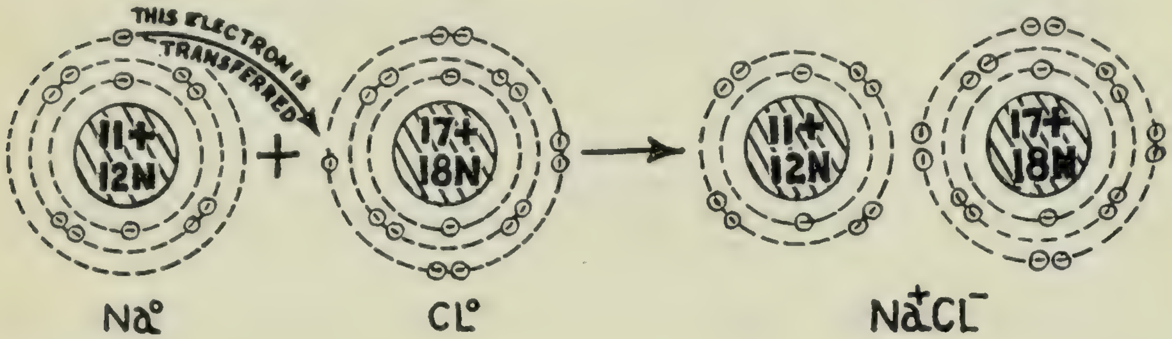


FIG. 110—THE FORMATION OF SODIUM CHLORIDE FROM ITS ELEMENTS

Compounds, like sodium chloride, formed by an exchange of electrons are called *polar* compounds. When such compounds are dissolved in water their molecules are dissociated (broken up) into ions. This can be expressed in an equation as follows:

$$\underset{\substack{\text{molecule of}\\\text{sodium chloride}}}{\mathbf{NaCl}} \rightleftharpoons \underset{\substack{\text{sodium}\\\text{ion}}}{\mathbf{Na^+}} + \underset{\substack{\text{chloride}\\\text{ion}}}{\mathbf{Cl^-}}$$

This process is called *ionization* and only polar compounds do this. The polar compounds include only acids, bases, and salts. They are sometimes known as *electrolytes* because they conduct the electric current.

10. Sharing Electrons

Many atoms, instead of gaining or losing electrons, may combine by sharing electrons, always in one or more pairs. In the molecules of the compounds so produced, the shared pairs are common to the outer orbits of all the atoms concerned. The combination of two hydrogen atoms to form a molecule of hydrogen is the simplest illustration of this type of reaction. Examination of Fig. 111 shows that one pair of electrons is shared by the two hydrogen atoms in the hydrogen molecule.

That is, one pair of electrons is common to both orbits of the hydrogen atoms. The formation of methane, CH_4, by the direct combination of 4 hydrogen atoms with one carbon atom is another good illustration of this method of chemical combination. The carbon atom completes its outermost shell by sharing 4 pairs of electrons with 4 hydrogen atoms. This is also shown in Fig. 112. A more condensed way of expressing this type of reaction is by means of atomic symbols and dots (.).

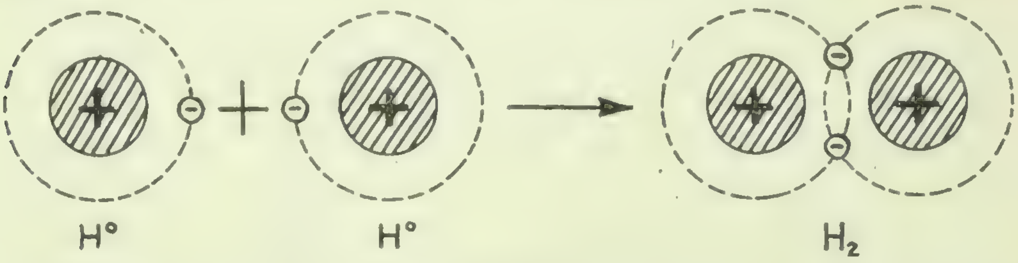


FIG. 111

A diagram to show the formation of a hydrogen molecule by the sharing of a pair of electrons with two hydrogen atoms.

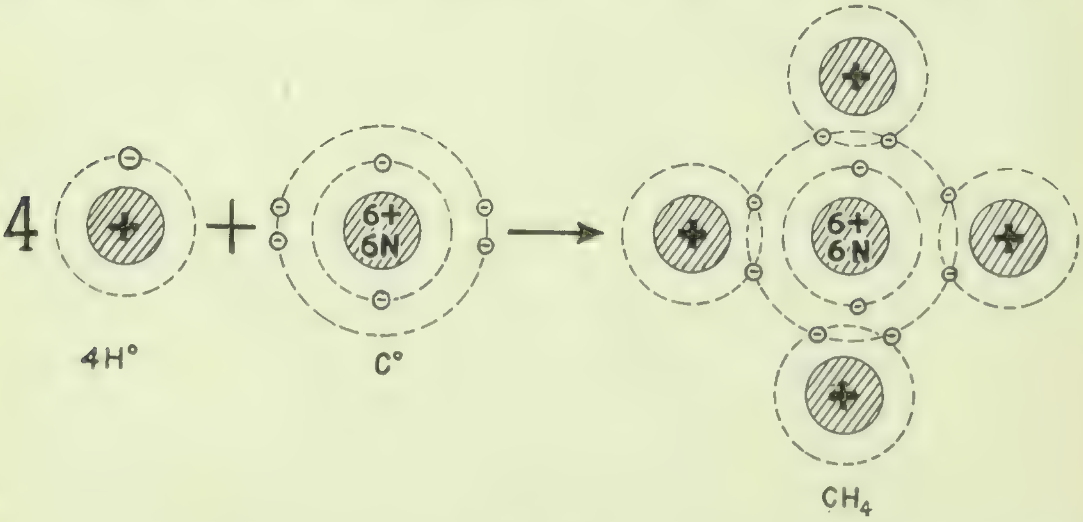


FIG. 112

A diagram to show the formation of a methane molecule by the sharing of four pairs of electrons with four hydrogen atoms.

The illustrations shown in Figs. 111 and 112 can be written as follows:

$$\underset{\text{hydrogen atom}}{H^{\cdot}} + \underset{\text{hydrogen atom}}{H^{\cdot}} \longrightarrow \underset{\text{hydrogen molecule}}{H : H}$$

$$\underset{\text{hydrogen atoms}}{4\ H^{\cdot}} + \underset{\text{carbon atom}}{:C:} \longrightarrow \underset{\text{methane molecule}}{\begin{array}{c} H \\ \cdot\cdot \\ H : C : H \\ \cdot\cdot \\ H \end{array}}$$

Compounds formed by the sharing of electrons are called *non-polar* compounds and they do not ionize in water. Non-polar compounds in solution do not conduct the electric current, and so they are often referred to as *non-electrolytes*.

If an atom shares one pair of electrons it has a valence of one. An atom which shares 2 pairs has a valence of 2. One which shares 3 pairs has a valence of 3 and an atom sharing 4 pairs would have a valence of 4.

It is interesting to know that the non-polar compounds are much more numerous than the polar compounds. Most organic compounds belong to the non-polar type and more than a quarter of a million of these compounds have been discovered.

11. Oxidation and Reduction from the Ionic and Electronic Viewpoint

The simplest case of oxidation is that of the combination of oxygen with a metal. The burning of magnesium ribbon in air is a good example of this.

$$2\ Mg + O_2 \longrightarrow 2\ MgO$$

The oxygen of the air is the oxidizing agent and the magnesium is the reducing agent, since, by definition, a reducing agent is a substance which is capable of being oxidized. Let us consider the above reaction from the ionic and electronic viewpoint. The magnesium atoms (Mg°) tend to lose 2 electrons, as they have 2 in their outermost orbit, and by doing so they become magnesium ions (Mg^{++}). On the other hand, oxygen atoms supplied by the oxygen molecules of the air tend to gain 2 electrons to complete their outermost orbit. The magnesium has been oxidized to magnesium oxide (MgO) and the oxygen of the air has been reduced to oxygen ions (O^{--}). The following equations are used to express these ideas.

$$(1)\ 2\ (Mg^\circ - 2\text{ electrons}) \longrightarrow 2\ Mg^{++}$$

$$(2)\ 2\ (\ 0^\circ\ + 2\text{ electrons}) \longrightarrow 2\ \ O^{--}$$

Equation (1) represents an oxidation reaction and (2), a reduction.

Another good example of oxidation and reduction is the action of hydrogen gas on hot cupric oxide. The molecular equation (ordinary) for this reaction is:

$$CuO + H_2 \longrightarrow Cu + H_2O$$

The ionic and electronic equations are:

(1) $\mathbf{Cu^{++}} + 2 \text{ electrons} \longrightarrow \mathbf{Cu^{\circ}}$
(2) $\mathbf{2\ (H^{\circ}} - 1 \text{ electron}) \longrightarrow \mathbf{2\ H^{+}}$

Equation (1) represents a reduction reaction and (2), an oxidation.

A study of these examples shows that *oxidation is a loss of electrons and reduction is a gain of electrons. An oxidizing agent is a substance which contains an atom or an ion capable of taking up electrons readily. A reducing agent is a substance which contains an atom or an ion capable of giving up electrons readily.* The active metals, such as sodium (Na), potassium (K), lithium (Li), which give up electrons most readily, are the most powerful reducing agents. On the other hand, nonmetallic elements like fluorine (F) and chlorine (Cl), whose atoms have a strong tendency to become negative ions by taking up electrons, are powerful oxidizing agents.

It is evident from the above consideration that oxidation and reduction does not necessarily involve oxygen. A few typical oxidation and reduction equations are given in Table 18 which shows that oxidation and reduction has a broader meaning than gain or loss of oxygen.

TABLE 18—SOME OXIDATION AND REDUCTION EQUATIONS

Molecular Equations	Electronic Equations	Type
1. $2Cu + O_2 \longrightarrow 2CuO$	$2(Cu^{\circ} - 2e) \longrightarrow 2Cu^{++}$ $2(O^{\circ} + 2e) \longrightarrow 2O^{--}$	Oxidation Reduction
2. $2FeCl_2 + Cl_2 \longrightarrow 2FeCl_3$	$2(Fe^{++} - 1e) \longrightarrow 2Fe^{+++}$ $2(Cl^{\circ} + 1e) \longrightarrow 2Cl^{-}$	Oxidation Reduction
3. $2Na + Cl_2 \longrightarrow 2NaCl$	$2(Na^{\circ} - 1e) \longrightarrow 2Na^{+}$ $2(Cl^{\circ} + 1e) \longrightarrow 2Cl^{-}$	Oxidation Reduction
4. $Fe + S \longrightarrow FeS$	$Fe^{\circ} - 2e \longrightarrow Fe^{++}$ $S^{\circ} + 2e \longrightarrow S^{--}$	Oxidation Reduction
5. $Sn + 2Cl_2 \longrightarrow SnCl_4$	$Sn^{\circ} - 4e \longrightarrow Sn^{++++}$ $4(Cl^{\circ} + 1e) \longrightarrow 4Cl^{-}$	Oxidation Reduction
6. $AlCl_3 + 3Na \longrightarrow 3NaCl + Al$	$Al^{+++} + 3e \longrightarrow Al^{\circ}$ $3(Na^{\circ} - 1e) \longrightarrow 3Na^{+}$	Reduction Oxidation

EXERCISES

1. Compare Dalton's idea of the atom with that of the modern chemist.
2. Write notes on protons, electrons and neutrons.
3. Discuss the following topics briefly: nucleus, electron orbits, and atomic numbers.
4. Draw the electron orbits for the atoms of the following elements: H, C, N, O, Ne, Na, and Cl.
5. (a) Discuss carefully the relationship between electrons and chemical activity.
   (b) Draw the diagrams for the formation of LiCl and $MgCl_2$.
6. (a) Draw the diagrams for the following molecules: H_2, O_2, CO_2, and CH_4.
   (b) What is the difference between a polar and a non-polar molecule?
7. Write electronic equations for the following molecular equations:

   (1) $Zn + S \longrightarrow ZnS$

   (2) $S + O_2 \longrightarrow SO_2$

   (3) $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2 \uparrow$

   (4) $H_2 + Cl_2 \longrightarrow 2\,HCl$

salt producer)

CHAPTER XXIX

CHLORINE—A TYPICAL HALOGEN

1. Occurrence

The halogen family of elements includes fluorine, chlorine, bromine, and iodine. These distinctly non-metallic elements combine readily with metallic elements to form salts, which are known as the *halides*. For this reason, these elements are called *halogens* which means "salt producers."

Chlorine, because of its activity, does not occur free in nature. It does, however, occur in large quantities in combination with other elements. The chief source is common salt, sodium chloride, NaCl, which is found in large deposits in various parts of the world. Magnesium chloride, $MgCl_2$, and potassium chloride, KCl, are both abundant chlorine compounds. Sea water contains about three per cent of sodium chloride, as well as smaller amounts of the chlorides of calcium, magnesium, and potassium.

FIG. 113—CARL WILHELM SCHEELE (1742–1786), A FAMOUS SWEDISH CHEMIST, WHO DISCOVERED CHLORINE

2. Preparation

(1) OXIDATION OF HYDROCHLORIC ACID BY MANGANESE DIOXIDE. The usual laboratory method for the preparation of chlorine is exactly the same as that used by the Swedish chemist, Scheele, in 1774. This consists of heating gently a mixture of manganese dioxide, MnO_2, and concentrated hydrochloric acid, HCl. Since chlorine is moderately soluble in water, and heavier than air, it is collected by the upward displacement of air (see Fig. 114). The reaction probably proceeds in two stages: the first, the formation of a higher chloride of manganese,

$$4\,HCl + \underset{\substack{\text{manganese}\\ \text{dioxide}}}{MnO_2} \longrightarrow \underset{\substack{\text{manganic}\\ \text{chloride}}}{MnCl_4} + 2\,H_2O$$

This compound is unstable, and so breaks up at once:

$$MnCl_4 \longrightarrow \underset{\substack{\text{manganous}\\ \text{chloride}}}{MnCl_2} + Cl_2\uparrow$$

The combined reactions may be represented by one equation:

$$4\ HCl + MnO_2 \longrightarrow MnCl_2 + Cl_2 + 2\ H_2O$$

This is an *oxidation* and *reduction* reaction. The MnO_2 is not a catalyst but it is an *oxidizing agent* because it furnishes the HCl molecules with oxygen atoms, which convert the hydrogen atoms in the HCl molecules into H_2O molecules. The HCl, of course, is a *reducing agent* because it removes oxygen from MnO_2.

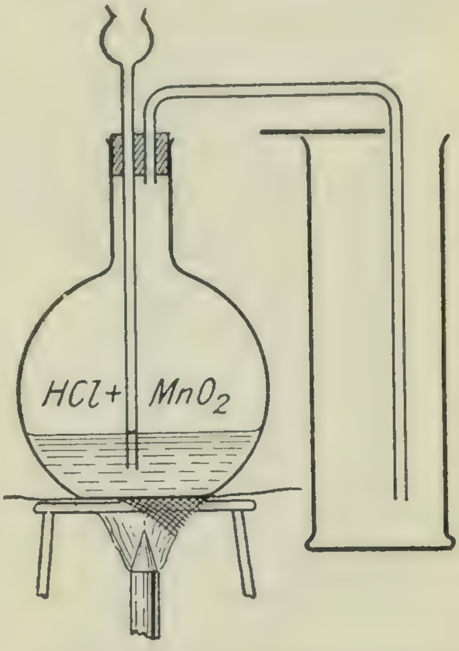


FIG. 114—THE LABORATORY PREPARATION OF CHLORINE

The above reaction is a good one to illustrate that oxidation and reduction can be considered from the electronic viewpoint. The manganese ion in MnO_2 has a charge of 4 positive and, when it comes in contact with concentrated HCl, it gains electrons from the chloride ions to be reduced to a charge of 2 positive. The chloride ions give up their electrons to become chlorine atoms which are electrically neutral. The chlorine atoms form non-polar chlorine molecules through the sharing of one pair of electrons by two atoms. The electronic-ionic equations for this reaction are given below:

$$Mn^{++++} + 2 \text{ electrons} \longrightarrow Mn^{++} \text{ (Reduction)}$$

$$2\ (Cl^- - 1 \text{ electron}) \longrightarrow 2\ Cl^\circ \text{ (Oxidation)}$$

$$\underset{\text{atoms}}{2\ Cl^\circ} \text{ (share 1 pair of electrons)} \longrightarrow \underset{\text{a molecule}}{Cl_2}$$

(2) OXIDATION OF HYDROCHLORIC ACID BY OTHER OXIDIZING AGENTS. Other oxidizing agents may be used in place of MnO_2, as is shown by the following equations:

$$PbO_2 + 4\ HCl \longrightarrow PbCl_2 + Cl_2\uparrow + 2\ H_2O$$

$$2\ KMnO_4 + 16\ HCl \longrightarrow 2\ KCl + 2\ MnCl_2 + 5\ Cl_2\uparrow + 8\ H_2O$$

$$K_2Cr_2O_7 + 14\ HCl \longrightarrow 2\ KCl + 2\ CrCl_3 + 3\ Cl_2\uparrow + 7\ H_2O$$

(3) ELECTROLYSIS OF A SODIUM CHLORIDE SOLUTION. This is the chief commercial method of preparing chlorine. It consists of passing a direct *electric current* through a concentrated

sodium chloride solution, known as brine. The method will be explained in detail later when the preparation of sodium hydroxide, NaOH, is considered (see page 309). The electrolysis of a sodium chloride solution can be conducted in the laboratory by means of the apparatus shown in Fig. 115. Chlorine gas is formed at the positive electrode, known as the anode, and hydrogen at the negative electrode, called the cathode. Sodium hydroxide, caustic soda, NaOH, is also formed around the cathode and its presence is indicated by the soapy feel of the solution near this electrode as well as by the fact that the liquid at this location turns red litmus blue. A complete explanation of this reaction cannot be given until the student understands the theory of ionization, which has not yet been considered, and therefore, this will be discussed later. For the present, the following equation can be used to explain the reaction:

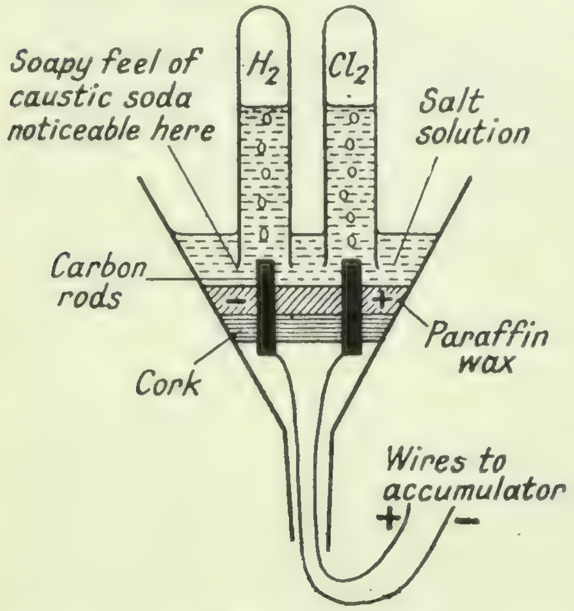


Fig. 115—The Electrolysis of Brine in the Laboratory

$$2\ \mathrm{NaCl} + 2\ \mathrm{H_2O} + \underset{\text{direct current}}{\mathrm{D.C.}} \longrightarrow \underset{\text{sodium hydroxide}}{2\ \mathrm{NaOH}} + \mathrm{H_2}\uparrow + \mathrm{Cl_2}\uparrow$$

It is noticed that besides the chlorine a valuable by-product, sodium hydroxide, is produced. The hydrogen formed also has commercial value. This process of producing chlorine commercially is used whenever electric current can be secured at a low cost.

3. Physical Properties

(1) Chlorine is a greenish-yellow *gas.*

(2) It possesses a very disagreeable odour.

(3) The gas is about two and one-half times as heavy as air, a litre weighing 3.22 grams.

(4) Chlorine is moderately soluble in water, a litre of water at 20° C. dissolving about 2.26 litres of chlorine.

(5) It may be easily condensed to a golden yellow liquid. This can be done at 20° C. under a pressure of about 7 atmos-

pheres. The liquid is stored in strong cylinders lined with lead, which are available in 10 lb. and 150 lb. cylinders. A large cylinder is shown in Fig. 116. In large quantities chlorine is shipped in unit tank cars of 16 tons and 30 tons and multi-unit tank cars of fifteen one-ton containers.

Fig. 116

A chlorine cylinder, which holds about 150 lbs. of the element.

4. Chemical Properties

The arrangement of the electrons in the chlorine atom (2,8,7) indicates that the element should readily pass into a stable form by taking on an additional electron. When such a change occurs the atom (Cl°) is converted into an ion (Cl^-) with a single negative charge. When chlorine is placed in contact with other elements whose atoms tend to give up electrons, there is a transfer of an electron to the chlorine atoms with great readiness. As a result of this tendency chlorine is a very active element, and most of the reactions of chlorine are due to this fact.

(1) Chlorine Does Not Burn in Air or Oxygen. That is, chlorine does not combine directly with oxygen. Oxides of chlorine can be produced but they are formed by the decomposition of certain chlorine compounds.

(2) The Gas Supports Combustion. Powdered antimony, Sb, combines readily with chlorine, giving off heat and light.

$$\underset{\text{antimony}}{2\ Sb} + 3\ Cl_2 \longrightarrow \underset{\substack{\text{antimony}\\\text{trichloride}}}{2\ SbCl_3}$$

It is hard to believe that common salt is produced when chlorine is passed over molten sodium. However, such is the case, and the action is accompanied by the evolution of much heat and light.

$$2\ Na + Cl_2 \longrightarrow 2\ NaCl$$

Iron, copper, and zinc, when heated, combine readily with chlorine. Each reaction gives off appreciable amounts of light and heat.

$$\underset{\text{}}{2\,Fe + 3\,Cl_2} \longrightarrow \underset{\text{ferric chloride}}{2\,FeCl_3}$$

$$Cu + Cl_2 \longrightarrow \underset{\text{cupric chloride}}{CuCl_2}$$

$$Zn + Cl_2 \longrightarrow \underset{\text{zinc chloride}}{ZnCl_2}$$

It must be remembered that chlorine does not support ordinary combustion. A burning splinter of wood is extinguished when placed in a jar of chlorine.

(3) CHLORINE COMBINES WITH HYDROGEN. A jet of burning hydrogen, when placed in chlorine, continues to burn, producing hydrogen chloride gas. This is shown in Fig. 117.

$$H_2 + Cl_2 \longrightarrow 2\,HCl$$

A mixture of hydrogen and chlorine does not react when kept in the dark. In *diffused sunlight*, the two gases combine slowly. In *direct sunlight*, they unite with explosive violence.

The affinity of chlorine for hydrogen is so great that it even removes hydrogen from certain hydrogen compounds. For example, if a piece of filter paper is saturated with warm turpentine, $C_{10}H_{16}$, and thrust into a jar of chlorine, the chlorine removes the hydrogen from the hydrocarbon, leaving a cloud of black smoke (carbon) in the bottle. The reaction is usually accompanied by a flash of light.

$$\underset{\text{Turpentine}}{C_{10}H_{16}} + 8\,Cl_2 \longrightarrow 16\,HCl \uparrow + 10\,C \downarrow$$

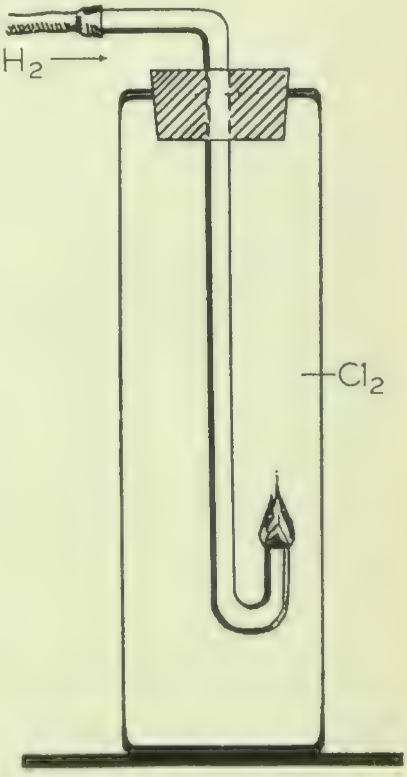


FIG. 117—HYDROGEN BURNING IN CHLORINE

The action on turpentine is an example of a *substitution* reaction, the carbon being replaced by the chlorine. If a lighted wax candle is lowered into a bottle of chlorine, it continues to burn with a smoky flame. The wax, being a mixture of paraffin hydrocarbons, is decomposed in the same way as turpentine.

(4) REACTS WITH WATER. Chlorine acts upon cold water, when dissolved in the latter, to form hydrochloric acid (HCl) and hypochlorous acid (HClO) according to the following equation:

$$H_2O + Cl_2 \rightleftharpoons HCl + \underset{\text{hypochlorous acid}}{HClO}$$

It has been found that with half-saturated chlorine-water at 10° C. (water containing about an equal volume of chlorine gas) about one-third of the chlorine is changed into the acids. Thus, chlorine-water (the solution) is a mixture containing dissolved chlorine and two acids.

The action between chlorine and water stops when one-third completed, because the two acids which are formed react with each other to reproduce chlorine and water (read the equation backwards). The reaction is a *reversible* one. When a solution of chlorine is exposed to sunlight, the hypochlorous acid decomposes and oxygen gas is liberated and escapes.

$$2\,HClO \longrightarrow 2\,HCl + O_2\uparrow$$

From the above it is evident that a water solution of chlorine must be kept in the dark, since otherwise, after a time, only a dilute solution of hydrogen chloride remains.

(5) CHLORINE IS A POWERFUL BLEACHING AND DISINFECTING AGENT. The so-called bleaching action of "chlorine" is due to the oxidation of the coloured material by hypochlorous acid ($HClO$). Chlorine and the dye in the cloth, when even moderately dry, do not react with each other. This may be shown by placing a piece of dry coloured calico in a bottle of dry chlorine. Even after several hours no bleaching takes place. If, however, either the calico or the chlorine is moist, the colour of the calico disappears almost at once. It is the hypochlorous acid which is the active oxidizing agent and it oxidizes the coloured dye in the cloth to a colourless compound. Hypochlorous acid is a more active bleaching agent than is ozone (O_3) or hydrogen peroxide (H_2O_2).

Moist chlorine is also a good disinfectant because the hypochlorous acid in the water oxidizes germs to harmless substances.

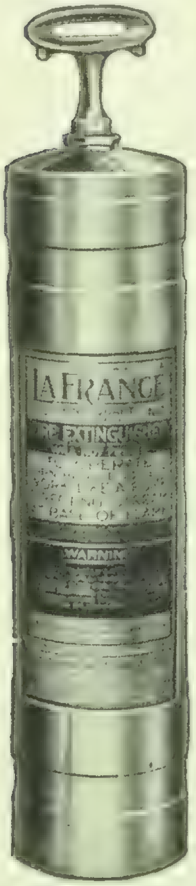
(6) POISONOUS. The gas, when inhaled, attacks the membranes of the nose and throat, producing coughing, inflammation, and even death. When there is one part of chlorine to ten thousand parts of air, the struggle for breath becomes acute, and a man would probably be put out of action in about five minutes.

5. Uses

(1) BLEACHING AGENT. The chief use of chlorine is as a bleaching agent. It is used for bleaching cotton, linen, wood pulp, and flour. Silk and wool are bleached by other methods, because chlorine hardens and destroys the fibres of these ma-

terials. The bleaching of cotton fabrics and wood pulp for paper require in North America alone several hundred tons of chlorine per day. The bleaching process is carried out in water solution and either chlorine-water, or bleaching powder ($CaOCl_2$) dissolved in water, is used.

(2) In Purifying Water. Chlorine is used extensively in the purification of water by municipalities both by itself and in the form of its compound with ammonia, chloramine ($ClNH_2$). Since its introduction for destroying disease-producing bacteria in water supplies, typhoid fever has been reduced to a minimum in many of the great cities of the world (see Fig. 64, page 105). About four pounds of chlorine per million gallons of water are sufficient to make city water supplies and swimming pools safe.



Courtesy of LaFrance Fire Engine and Foamite Ltd.

Fig. 118

A Carbon Tetrachloride Type Extinguisher

The vaporizing liquid is expelled in a continuous stream by a *manually operated pump.*

(3) To Make Bleaching Powder or Chloride of Lime. Chlorine reacts with slightly moist slaked lime, calcium hydroxide, $Ca(OH)_2$, to form bleaching powder, $CaOCl_2$, sometimes called "chloride of lime."

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$

Bleaching powder is a cheap and effective disinfectant. It is also a convenient bleaching agent.

(4) In Manufacturing Chlorine Compounds. Chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), which is used in fire extinguishers (see Fig. 118), and sulphur monochloride (S_2Cl_2) are a few examples of the many valuable chlorine compounds used in commerce. Duprene, one of the chief types of synthetic rubber, requires chlorine in its manufacture.

(5) In Warfare. Free chlorine was first used in World War I as a poison gas by the Germans on April 22, 1915. They concealed tanks of liquid chlorine in the front line trenches, and the substance was used in the form of gas clouds. As chlorine is heavier than air, the clouds were carried over the ground by the wind. It was soon found that greater damage could be done by "gases" (usually liquids) contained in shells which could be sent directly to the enemy's position.

Chlorine was not suitable for this purpose, but it was a constituent of most of the well-known toxic gases used in World War I. Among the most important were *phosgene*, carbonyl chloride ($COCl_2$), very deadly in its effects; chloropicrin, nitrochloroform ($C \cdot NO_2 \cdot Cl_3$), a tear and vomiting gas; and *mustard gas*, dichloro-diethyl-sulphide, $(Cl_2CH_4)_2S$, a burning and blistering compound.

(6) OTHER USES. Chlorine is also used in the preparation of many compounds which are needed in the explosive and dye industries. Liquid chlorine can be used in extracting gold from its ores, and also in recovering tin from old tin cans and scrap tin plate.

EXERCISES

1. (a) What is the meaning of the term halogen?
   (b) Make a list of the elements in the halogen family.
2. Write a note on the occurrence of chlorine.
3. Write electronic-ionic equations for the oxidation of hydrochloric acid by the following oxidizing agents: manganese dioxide, lead dioxide, and potassium permanganate.
4. Write the equation for the preparation of chlorine from common salt by electrolysis.
5. Is chlorine an active or an inactive element? Discuss from the viewpoint of the electronic structure of the atom.
6. What part does water take in the bleaching of cotton? Write equations to make your answer clear.
7. Why is chlorine not collected by the downward displacement of water?
8. (a) Tabulate *five* physical properties of chlorine.
   (b) Tabulate *five* chemical properties of chlorine. Write equations to illustrate.
9. Write a note on the uses of chlorine.

CHAPTER XXX

HYDROCHLORIC ACID

1. History and Occurrence

Hydrochloric acid, HCl, is a water solution of hydrogen chloride gas, and it is the most important halogen compound manufactured in chemical industry. Water solutions of hydrochloric acid were known from very early times and the pioneer chemists, known as the alchemists, prepared it by the action of sulphuric acid on salt. The pure, dry, gaseous acid was first prepared by Priestley in 1772. He called it *marine acid gas.* It occurs as free hydrogen chloride in the gases coming from *volcanoes.* The acid has been reported to be found in certain rivers in South America which flow through volcanic regions. Hydrochloric acid is also found in the gastric juice of the stomach in a concentration of about 0.3 per cent.

2. Preparation

(1) BY THE DIRECT COMBINATION OF HYDROGEN AND CHLORINE. These two gases combine readily, forming hydrogen chloride. This fact was forcibly brought home to the French chemists, Gay-Lussac and Thenard in 1809, who found upon exposing equal volumes of hydrogen and chlorine to sunlight that "they (the elements) suddenly inflamed with a very loud detonation, and the jars were reduced to splinters, and projected to a great distance." Some hydrochloric acid is manufactured in essentially the same way today, care, of course, being taken to avoid the "loud detonation" which destroyed the apparatus of the men who discovered this reaction.

$$H_2 + Cl_2 \longrightarrow 2\ HCl$$

Acid made commercially by this method, namely, by burning chlorine in hydrogen, is a water-white acid. It is essentially chemically pure (C.P.).

(2) BY THE ACTION OF CONCENTRATED SULPHURIC ACID ON SODIUM CHLORIDE. When a mixture of concentrated sulphuric acid and sodium chloride is heated, hydrogen chloride is readily evolved. The gas is collected by the upward displacement of air (Fig. 119). If the gas is allowed to pass into some water in

a bottle, as shown in the diagram, it dissolves in the water, forming hydrochloric acid. The reaction which takes place in the preparation of hydrogen chloride depends upon the temperature.

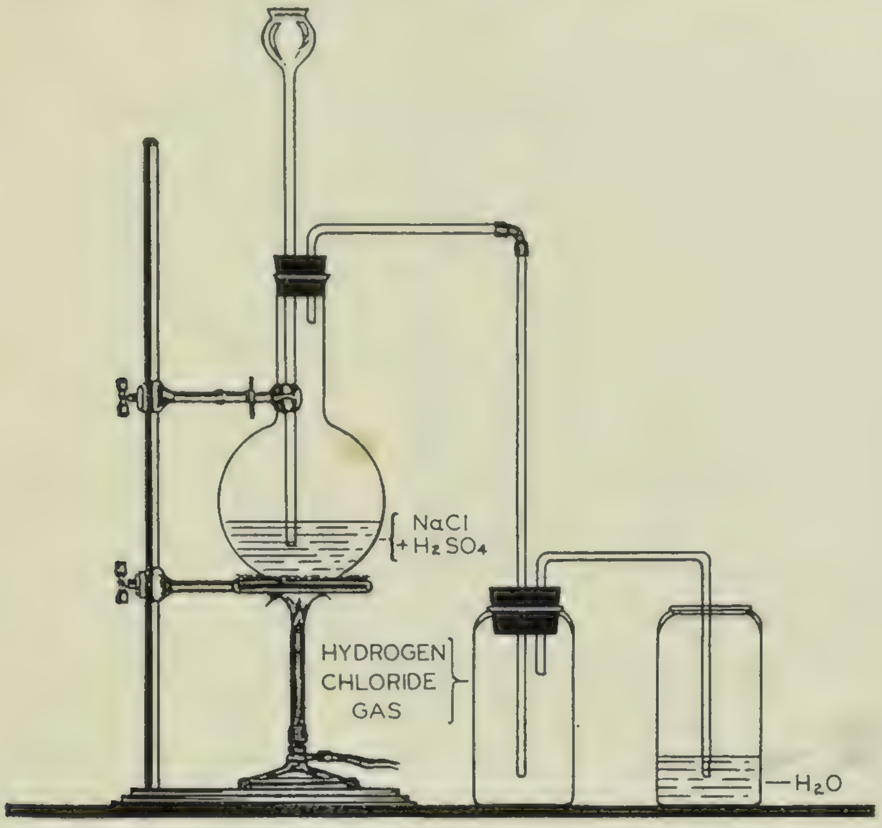


FIG. 119

The laboratory preparation of hydrogen chloride, showing the collection of the gas by the upward displacement of air, and also the formation of hydrochloric acid by passing the gas into water.

If the mixture of common salt and sulphuric acid is *heated gently*, the reaction is as follows:

(1) $$NaCl + H_2SO_4 \longrightarrow \underset{\text{sodium hydrogen sulphate}}{NaHSO_4} + HCl \uparrow$$

If an excess of sodium chloride is used and the mixture *heated strongly*, the reaction is as follows:

(2) $$2\ NaCl + H_2SO_4 \longrightarrow \underset{\text{sodium sulphate}}{Na_2SO_4} + 2\ HCl \uparrow$$

The *sodium hydrogen sulphate*, $NaHSO_4$, produced in reaction (1), is also known as *sodium bisulphate*. It is also called *sodium acid sulphate*, and it is an *acid salt* because it still contains a replaceable hydrogen atom in its molecule. A water solution of this salt turns blue litmus red.

The preparation of hydrogen chloride from salt and concentrated sulphuric acid illustrates a general method of making acids, namely, the action of concentrated sulphuric acid on the salt of the desired acid. In preparing hydrochloric acid, sodium chloride, rather than some other chloride, is used because it is the cheapest source of chlorine. Sulphuric acid is used for the following reasons:

(1) It has the highest boiling point of the most common acids (338° C.), and so it remains behind in the reaction flask, while the hydrogen chloride is driven off as a gas by gentle heating.

(2) The acid is a source of the hydrogen needed to produce hydrogen chloride.

(3) It is a dehydrating agent, removing the water from the gas before it is driven off.

(4) Sulphuric acid is relatively cheap.

The action of sulphuric acid on salt is also the chief industrial method of producing hydrochloric acid. The operation is carried out by heating the mixture of salt and sulphuric acid in large retorts or furnaces. The hydrogen chloride is passed into water in which it dissolves in large quantities. It is known commercially as *muriatic* acid and acid made by this method has a pale yellow colour. It is shipped in glass carboys of 12-gallon capacity, set in a wooden protecting box, or in rubber-lined wooden tanks, four tanks to a flat railroad car. The ordinary commercial acid contains about 32 per cent pure hydrogen chloride by weight.

3. Physical Properties of Hydrogen Chloride

(1) Hydrogen chloride is a colourless gas.

(2) It has a sharp, choking odour.

(3) The gas is heavier than air.

(4) It is extremely soluble in water, one litre of water dissolving about 500 litres of the gas at room temperature (Fig. 120).

(5) Hydrogen chloride absorbs and condenses the moisture of the air, causing white fumes which consist of very small droplets of hydrochloric acid.

(6) The gas is readily liquefied.

4. Chemical Properties of Hydrogen Chloride

(1) It is a very stable compound.

(2) Hydrogen chloride does not burn.

(3) It does not support combustion.

(4) The gas can be oxidized to form water and chlorine:

$$4\ HCl + O_2 \rightleftharpoons 2\ H_2O + 2\ Cl_2$$

(5) Hydrogen chloride gas is very irritating to the membrane of the nose and throat and, if inhaled in large quantities, serious results may follow.

(6) One of the most interesting chemical properties of the gas is its reaction with ammonia gas. When these two compounds come together, a dense white smoke is at once produced. The smoke is due to very fine particles of ammonium chloride which is formed when the two substances react.

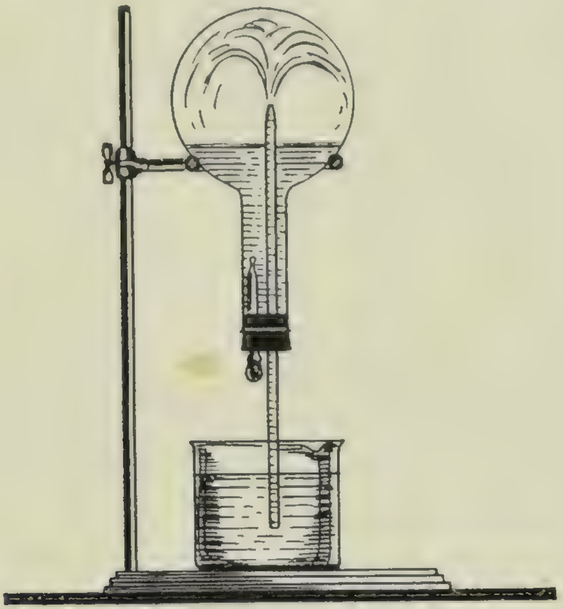


FIG. 120

The hydrogen chloride fountain experiment shows that this gas is very soluble. The flask is filled with dry hydrogen chloride gas and arranged as shown above. The medicine dropper contains a small amount of water, and when the rubber bulb is pinched, a few drops of water are forced into the flask. This small amount of water dissolves such a large quantity of the gas that a partial vacuum is formed in the flask. The outside pressure of the air then forces the water in the beaker up through the tube to produce a fountain.

$$HCl + NH_3 \longrightarrow \underset{\text{ammonium chloride}}{NH_4Cl}$$

This reaction is used as a chemical test for hydrogen chloride gas as well as for ammonia.

(7) Hydrogen chloride ionizes in water to produce hydrogen ions (H^+) and chloride ions (Cl^-). This can be expressed as follows:

$$HCl \rightleftharpoons H^+ + Cl^-$$

It is for this reason that hydrogen chloride in water produces an acid, which is known as hydrochloric acid. The chief properties of all acids, in solution, are due to the presence of hydrogen ions.

5. The Chief Properties of Hydrochloric Acid

(1) Chemically pure hydrochloric acid is a colourless solution of hydrogen chloride in distilled water.

(2) It is a typical acid, and shows all the characteristics of that group of compounds. It turns blue litmus red and it has a sour taste. The dilute acid also reacts with metals above hydrogen in the electromotive series, to form chlorides and hydrogen.

$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2\uparrow$$
$$2\,Al + 6\,HCl \longrightarrow 2\,AlCl_3 + 3\,H_2\uparrow$$

Hydrochloric acid also neutralizes bases, forming salts and water.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$
$$Ca(OH)_2 + 2\,HCl \longrightarrow CaCl_2 + 2\,H_2O$$

(3) Concentrated hydrochloric acid is a reducing agent. For example, it reduces manganese dioxide to produce chlorine.

$$MnO_2 + 4\,HCl \longrightarrow MnCl_2 + Cl_2\uparrow + 2\,H_2O$$

6. Chlorides

A chloride is a salt of hydrochloric acid. It contains a metal, or a metallic radical (like NH_4), combined with chlorine. Zinc chloride ($ZnCl_2$) and ammonium chloride (NH_4Cl) are typical chlorides. All the common chlorides are soluble in water, with the exception of silver chloride ($AgCl$), mercurous chloride ($HgCl$), and lead chloride ($PbCl_2$).

7. The Chemical Test for a Chloride

The addition of a water solution of silver nitrate ($AgNO_3$) to a soluble chloride, such as sodium chloride, produces a white precipitate of silver chloride ($AgCl$).

$$NaCl + AgNO_3 \longrightarrow AgCl\downarrow + NaNO_3$$

The precipitate is insoluble in dilute nitric acid (HNO_3) but it is soluble in an excess of ammonium hydroxide (NH_4OH). The precipitate ($AgCl$) turns purple on standing in sunlight. This test is a very sensitive one and it often shows the presence of chlorides in ordinary drinking water.

8. Uses of Hydrochloric Acid

(1) The chief industrial use of hydrochloric acid is in cleaning metals before they are coated with tin or galvanized (dipped in

molten zinc). This method of cleaning metals is known as "pickling." Tinsmiths and plumbers also use commercial hydrochloric acid (muriatic) to clean metals before soldering.

(2) It is used in medicine as an aid to digestion.

(3) The acid is used in the manufacture of glue.

(4) Hydrochloric acid is employed in the making of glucose and gelatin.

(5) It is used to make chlorides.

$$\mathbf{Fe + 2\,HCl \longrightarrow FeCl_2 + H_2\uparrow}$$

(6) The acid is necessary in the manufacture of certain dyes.

EXERCISES

1. Write a note on the occurrence of hydrochloric acid.
2. Describe with the aid of a labelled diagram the laboratory preparation of hydrogen chloride from common salt and sulphuric acid.
3. Tabulate five physical and four chemical properties of hydrogen chloride.
4. Write a note on chlorides.
5. Describe the chemical test for a chloride. Give the equation.
6. Write a note on the uses of hydrochloric acid.
7. Calculate the weight of hydrogen chloride necessary to neutralize 100 g. sodium hydroxide. What weight of salt would be produced?

Chapter XXXI

SULPHUR

1. Importance and Occurrence

Sulphur, occurring in the free state in large deposits, was one of the first of the chemical elements to become known to man. It is mentioned in the Bible as *brimstone*, which means the stone that burns.

Sulphur is of great importance in industry. Several million tons of this solid element are used every year throughout the world. Much of this vast quantity of sulphur is used to produce sulphuric acid, a chemical which plays a very important part in the preparation of a large number of important commercial materials. Sulphur dioxide is another important compound of sulphur and it is used for disinfecting, bleaching, and refrigeration. In addition to being used in the production of sulphuric acid and sulphur dioxide, sulphur, in the free state, is used in the rubber industry and in the preparation of many other chemicals and articles of commerce.

Sulphur occurs widely distributed in nature in both the free and the combined states. Large deposits of *free* or *native* sulphur are found in Texas, Louisiana, and Sicily (until recent years the source of most of the world's supply). Sulphur also occurs in many other places, such as Japan, Mexico, and Iceland. It is often found around the rims of craters and near volcanoes.

Sulphur in the *combined* state is much more abundant and widely distributed than native sulphur. It occurs chiefly as *sulphides* and *sulphates*. Sulphides contain sulphur and one other element, usually a metal. Many sulphide minerals are of great industrial importance, such as iron pyrites, or "fool's gold" (FeS_2), copper pyrites, or chalcopyrite ($CuFeS_2$), zinc sulphide, or zinc blende (ZnS), lead sulphide, or galena (PbS), and mercuric sulphide, or cinnabar (HgS). Hydrogen sulphide, or sulphuretted hydrogen, is present in the so-called sulphur waters and in certain volcanic gases.

Sulphates, or salts of sulphuric acid, are found in nature in very large quantities. Some of the most important of these compounds are: calcium sulphate, or gypsum ($CaSO_4 \cdot 2H_2O$), barium sulphate, or barite ($BaSO_4$), and magnesium sulphate, or Epsom salts ($MgSO_4 \cdot 7H_2O$). Millions of tons of gypsum are removed from the earth every year. This important sulphur compound is used in agriculture, in the manufacture of plaster-of-Paris, gypsum building board and as a filler in the manufacture of paper.

Sulphur compounds are also found quite widespread in the plant and animal kingdoms. They are found in garlic, onions, mustard, hair, wool, the blood, and bile. Sulphur is present as a constituent of certain proteins, such as egg albumen or casein of milk. It is also present in petroleum and coal.

2. Extraction of Sulphur

Until the year 1902, 90 per cent of the world's supply of sulphur came from Sicily. The mixture of the element with rocks and earth was heated to melt the sulphur, which flowed away from the impurities. The crude sulphur was finally purified by distillation from iron retorts, the fumes being passed into large brick chambers as shown in Fig. 121. At first, part of the gas condensed on the walls as a fine powder, which is known as "flowers of sulphur." As the condensing chamber became hot the sulphur melted and ran down the sides of the

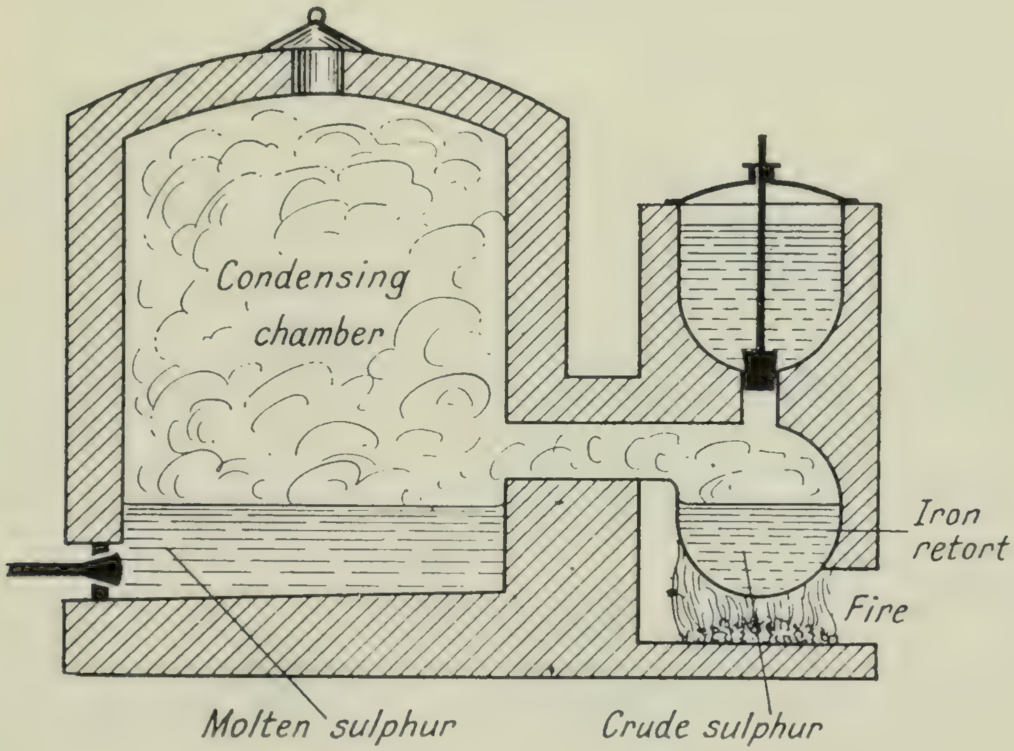


FIG. 121—THE PURIFICATION OF SULPHUR BY DISTILLATION FROM IRON RETORTS

chamber to the floor. It was then run into round moulds where it cooled to a solid which is called *roll sulphur*.

Vast quantities of sulphur occur in Louisiana and Texas. These deposits are deep down in the earth's crust, at depths of 600 to 1100 feet, and the deposits average 125 feet in thickness. The sulphur is brought to the surface by a process known as the *Frasch Process*, which was devised by an American engineer,

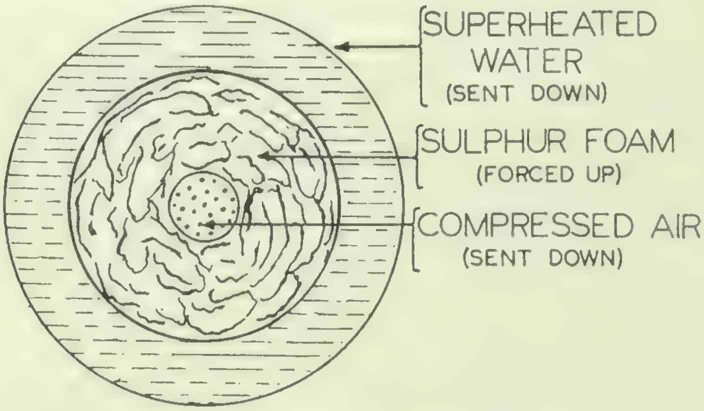
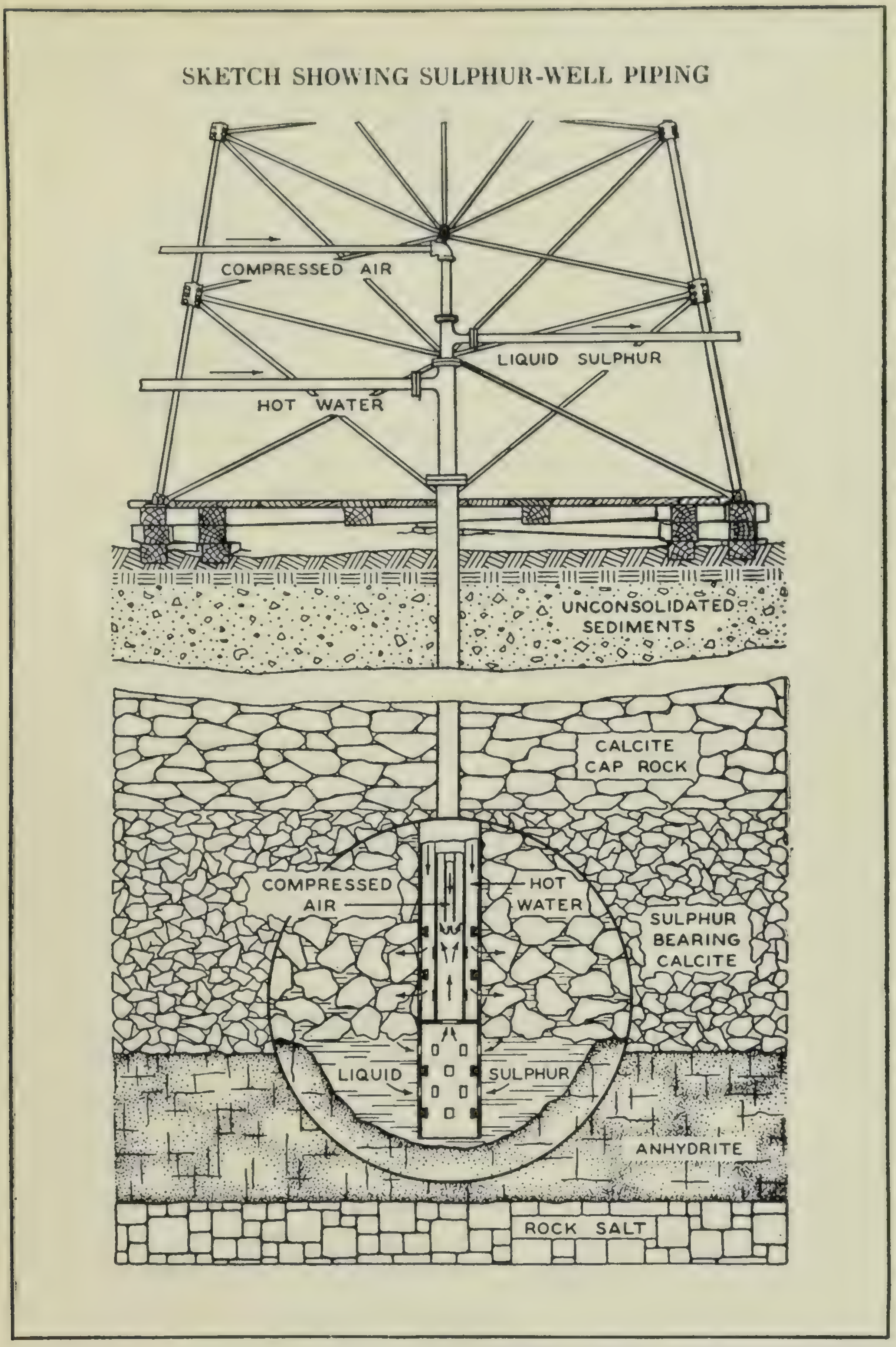


FIG. 122—CROSS-SECTION OF THE THREE CONCENTRIC PIPES IN FRASCH PROCESS

Courtesy of The Texas Gulf Sulphur Company

FIG. 123—SULPHUR READY FOR LOADING

Sulphur is stored in vats, each of which may be 1200 feet long, 175 feet wide and 50 feet high. Each vat may contain one-half million tons of sulphur. The vats are broken down for loading.



Courtesy of The Texas Gulf Sulphur Company

Fig. 124

Herman Frasch in 1902 (see Fig. 124). A well, similar to those used in the petroleum industry, is sunk through the clay, soil, and other materials to the deposit. Three concentric pipes (1, 3, and 6 inches in diameter, respectively) are placed in the well (see Fig. 122). Superheated water, under 100 pounds pressure and at a temperature of 171° C. (340° F.) is forced down through the outermost pipe. This causes the sulphur (melting point 114.5° C. or 235° F.) in the deposit to melt. From 10 to 50 tons of water are needed for the production of each ton of sulphur. Compressed air (500 pounds per square inch) is then forced down through the innermost pipe, mixing with the sulphur to make it foamy and light. This mixture of air, water, and melted sulphur is forced up the middle pipe in a frothy stream. The molten sulphur is run into pits heated by steam so that the sulphur remains molten. Here separation from the water takes place and the molten sulphur is then pumped into large wooden vats 1200 feet long, 175 feet wide and 50 feet high, where it solidifies, as shown in Fig. 123. The result is an enormous block of sulphur, weighing thousands of tons and quantities of sulphur, when needed, are blasted off by dynamite. A part of the hot water is recovered from the deposit by neighbouring "bleed wells" and the heat from this water can be used in the refining process. Continuous operation in the Frasch process is essential, because, if stopped, the molten sulphur in the deposit solidifies and "freezes" the pipes in each hole. The output for each well is about 500 tons per day and the sulphur is 99.5 per cent pure, which for most industrial uses, requires no further refining.

3. Physical Properties

Sulphur is an *allotropic* element; that is, it exists in two or more distinct forms in the same state. Other allotropic elements are: carbon, oxygen, phosphorus, arsenic, tin, antimony and boron. There are two *crystalline* forms of sulphur, *rhombic* and *monoclinic* (prismatic). The rhombic form is prepared by dissolving sulphur in carbon disulphide, which evaporates quickly, leaving behind crystals of this variety of sulphur (see Fig. 125). Monoclinic or prismatic crystals may be prepared by melting sulphur very slowly, and then pouring the molten sulphur into a folded filter paper. As soon as crystals extend from the sides to the centre of the cone, the surface crust is broken and that portion of the sulphur, which is still liquid, is poured into a beaker of water. The filter paper is opened up at once and the long needle-like crystals may be examined with a magnifying glass (see Fig. 125). When liquid sulphur is heated almost to its boiling point and then cooled quickly by pouring the molten mass into cold water, it is changed into a soft, rubbery, amorphous (non-crystalline) material. This is known as *plastic* sulphur (see Fig. 125). On standing for several days, at room temperature, the plastic variety changes to a hard and brittle solid, because of the slow change of the material into the rhombic form. The monoclinic or prismatic crystals also change to rhombic on standing for a few days. These three forms of sulphur, because of differences in atomic arrangement and energy content, differ widely in their *physical properties*. They have, however, the *same chemical properties*. A comparison of their chief physical properties is shown in Table 19.

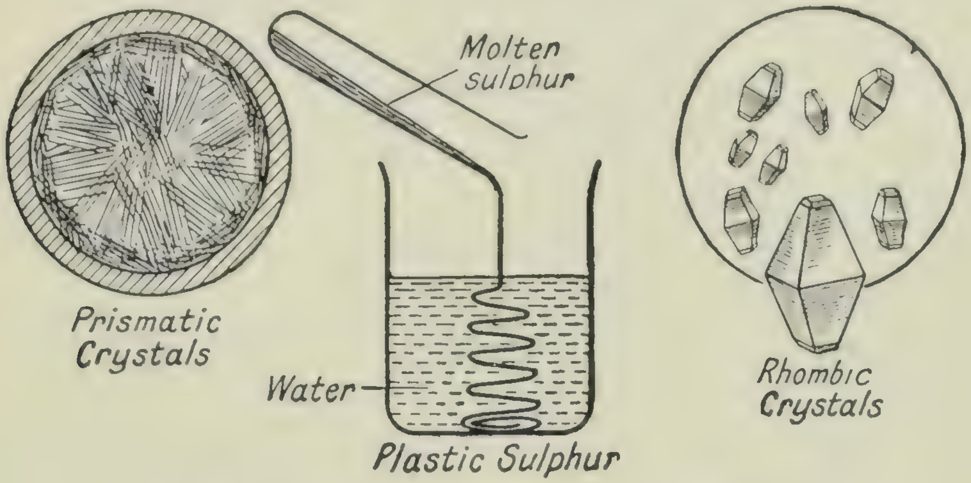


FIG. 125—ALLOTROPIC FORMS OF SULPHUR

A study of the stability of the three forms of sulphur shows that at 96° C. the rhombic and monoclinic forms can exist together unchanged for any length of time. Above 96° C. the rhombic slowly changes to the monoclinic, whereas below 96° C. the monoclinic slowly changes to the rhombic. This temperature, 96° C., is called the *transition point* of rhombic and monoclinic sulphur.

There are some interesting changes in sulphur with change of temperature. When the rhombic and monoclinic forms of sulphur are heated to their melting points they change from the solid state to a thin, straw-coloured liquid. If the heating is continued, the liquid becomes darker and thicker, until a jelly-like, viscous material is produced at a temperature of about 230° C. The material is so viscous at this temperature that it will not pour from a beaker. Above 230° C., the liquid again becomes thin (less viscous), although remaining dark in colour.

TABLE 19—A COMPARISON OF THE PHYSICAL PROPERTIES OF THE THREE FORMS OF SULPHUR

	Rhombic	Monoclinic	Plastic
Colour	lemon-yellow	honey-yellow	amber
Type of Crystal	rhombic	needle-like	non-crystalline
Specific Gravity	2.06	1.96	varies
Solubility	soluble in carbon disulphide	soluble in carbon disulphide	Insoluble in carbon disulphide
Melting Point	114.5° C.	119.0° C.	Indefinite
Stability	Stable below 96° C.	Stable between 96° C. and 114° C. Changes to rhombic below 96° C.	Stable above 114° C. Changes to rhombic when cooled.

At 445° C., it reaches its boiling point and a yellow vapour is given off at that temperature. When the vapour cools, the same changes take place in the reverse order.

4. Chemical Properties

Sulphur, like oxygen, has six electrons in the outermost orbit of its atom. This means that both oxygen and sulphur atoms tend to take up two electrons to complete their outermost orbits, and so they will both show a negative valence of two. Thus, even though these two elements are not alike in physical properties, they resemble each other to a marked degree in their chemical properties. Thus, sulphur reacts with most metals, producing a group of binary compounds called sulphides. These correspond to the oxides of the metals. The chief chemical properties of sulphur are as follows:

(1) *It burns in air* with a purple flame.

$$S + O_2 \longrightarrow SO_2$$

(2) *Sulphur supports combustion.* For example, iron and copper, if very hot, actually burn in hot sulphur vapour. This is an excellent example of combustion without oxygen.

$$\mathrm{Fe + S \longrightarrow FeS}$$
$$\mathrm{Cu + S \longrightarrow CuS}$$

(3) *It combines with hydrogen slowly,* forming hydrogen sulphide gas.

$$\mathrm{H_2 + S \longrightarrow H_2S}$$

(4) *Sulphur combines with metals forming sulphides.*

$$\mathrm{2\,Ag + S \longrightarrow \underset{\text{silver sulphide}}{Ag_2S}}$$
$$\mathrm{Hg + S \longrightarrow \underset{\text{mercuric sulphide}}{HgS}}$$
$$\mathrm{Zn + S \longrightarrow \underset{\text{zinc sulphide}}{ZnS}}$$

(5) *It also combines with certain non-metals.* For example, sulphur combines with chlorine, forming sulphur chloride, S_2Cl_2, which is used in vulcanizing rubber.

$$\mathrm{2\,S + Cl_2 \longrightarrow S_2Cl_2}$$

Sulphur vapour reacts with highly heated carbon, forming carbon disulphide, which is used as a solvent in industry for such materials as sulphur, rubber, waxes, resins, oils, and fats.

$$\mathrm{C + 2\,S \longrightarrow CS_2}$$

5. Uses

(1) The chief use of sulphur is in the manufacture of *sulphuric acid.* About one-half of the sulphur produced is used for this purpose.

(2) Sulphur plays an important part in the *vulcanizing of rubber.* This process consists in evaporating the water from the rubber latex (a white liquid obtained from the rubber tree) and heating the residue with a small percentage of sulphur. The material so produced is the rubber of commerce and it is much stronger and more elastic than native rubber. Hard rubber requires a greater percentage of sulphur.

(3) Sulphur is one of the components of *gunpowder* which is a mixture in certain proportions of sulphur, charcoal, and potassium nitrate (saltpetre).

(4) It is an *insecticide* and *fungicide.* For example, lime-sulphur spray, a deep red liquid, made by boiling a mixture of sulphur, slaked lime, and water, is sprayed on apple trees to kill insects and fungi (plant growths). Powdered sulphur is dusted on grape-vines to destroy pests.

(5) Sulphur is also used to produce *sulphites* which play an important part in the manufacture of paper.

(6) It is used in the manufacture of *matches*, *fire-works*, certain *dyes*, and *carbon disulphide* (see Fig. 126).

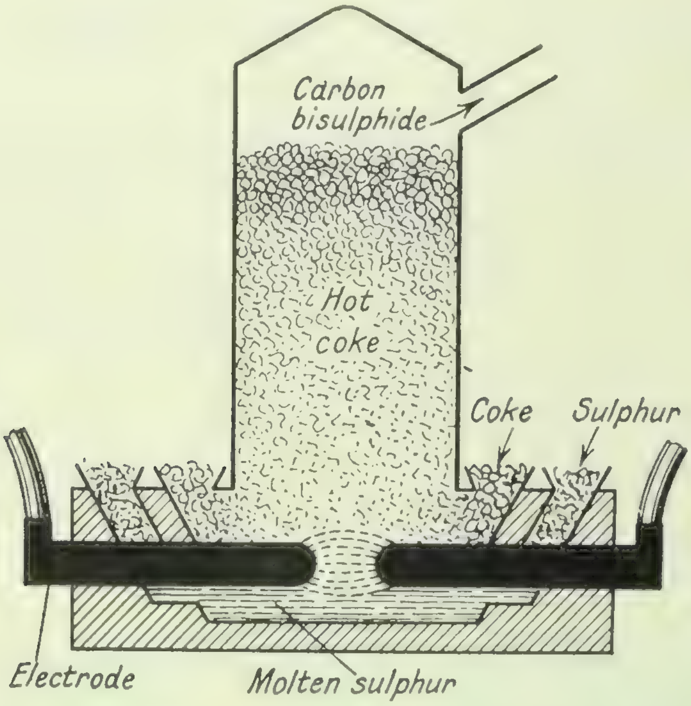


FIG. 126—THE MANUFACTURE OF CARBON DISULPHIDE

(7) Sulphur finds certain important uses in *medicine*. For example, it is necessary in the production of the important sulfa drugs, which have been a great aid to the medical profession in combating certain diseases.

EXERCISES

1. Write a note on the importance and occurrence of sulphur.
2. Describe the Frasch process in detail. Illustrate your answer with drawings.
3. (a) What is meant by an allotropic element?
   (b) Mention five allotropic elements.
4. Describe carefully the laboratory preparation of rhombic, monoclinic, and plastic sulphur. Mention two distinguishing characteristics of each.
5. Write a short note on the transition point of sulphur.
6. Describe the changes in sulphur with changes of temperature.
7. (a) Tabulate three chemical properties of sulphur. Give one equation to illustrate each property.
   (b) Make a list of five uses of sulphur.

CHAPTER XXXII

HYDROGEN SULPHIDE

1. Occurrence

Hydrogen sulphide is found in the gases escaping from *volcanoes.* It also occurs in the water of *sulphur springs.* Such waters are said to be beneficial for people suffering from rheumatism and similar ailments. Hydrogen sulphide is found wherever organic matter containing sulphur is decaying. Thus, it is present in *rotten eggs*, *decaying cabbages*, and *sewer gas.* It is also present in the gas given off by the *distillation of coal.*

2. Preparation

(1) DIRECT UNION. Hydrogen sulphide can be prepared by passing hydrogen through boiling sulphur.

$$H_2 + S \longrightarrow H_2S$$

(2) THE ACTION OF ACIDS ON SULPHIDES. Hydrogen sulphide is usually prepared in the laboratory by the action of a *dilute* acid, such as hydrochloric or sulphuric acid, upon a metallic sulphide. A number of sulphides (not all) may be used for the purpose, but ferrous sulphide, FeS, because of its cheapness, is generally used.

$$\mathbf{FeS + 2\ HCl \longrightarrow FeCl_2 + H_2S \uparrow}$$

In some laboratories large quantities of the gas are often needed for certain experiments, and so a special apparatus, called Kipp's apparatus, as shown in Fig. 127, is used.

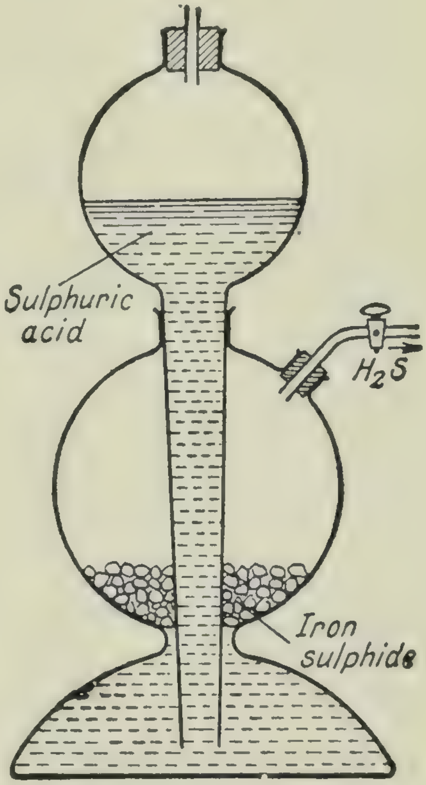


FIG. 127—KIPP'S APPARATUS FOR MAKING LARGE QUANTITIES OF HYDROGEN SULPHIDE GAS

3. Physical Properties

(1) Hydrogen sulphide is a *colourless gas.*
(2) It has the very offensive odour of rotten eggs.
(3) The gas is heavier than air.
(4) Hydrogen sulphide is moderately soluble in water. At 15° C., one litre of water dissolves a little more than 3 litres of the gas.

4. Chemical Properties

(1) Hydrogen sulphide *does not support combustion.*

(2) *It burns readily.* If there is a sufficient supply of oxygen, the combustion is complete, water and sulphur dioxide being formed.

$$2\ H_2S + 3\ O_2 \longrightarrow 2\ H_2O + 2\ SO_2 \uparrow$$

If the supply of oxygen is limited, as when the gas burns in a bottle, the products are water and free sulphur.

$$2\ H_2S + O_2 \longrightarrow 2\ H_2O + 2\ S \downarrow$$

It is quite probable that some of the sulphur found in volcanic regions was produced in this way.

(3) Hydrogen sulphide forms an acid when passed into water. This acid is a weak one and it is known as *hydrosulphuric acid.* When this acid is neutralized with a base, sulphides are formed.

$$2\ NaOH + H_2S \longrightarrow \underset{\text{(soluble in water)}}{Na_2S} + 2\ H_2O$$

(4) Hydrogen sulphide is a good *reducing agent.* As a rule free sulphur is produced when the gas reacts with an oxidizing agent. This is the case when hydrogen sulphide is mixed with sulphur dioxide.

$$2\ H_2S + SO_2 \longrightarrow 2\ H_2O + 3\ S \downarrow$$

Solutions of hydrogen sulphide are slowly oxidized by the oxygen of the air according to the following equation.

$$2\ H_2S + O_2 \longrightarrow 2\ H_2O + 2\ S \downarrow$$

(5) The gas reacts slowly with many metals, forming *metallic sulphides.* This may happen even with metals which are not much changed by oxygen. For example, the tarnishing of silverware is brought about by exposure to air containing traces of hydrogen sulphide. It has been shown recently that silver is not attacked by hydrogen sulphide at room temperature unless air and moisture are both present. The moisture dissolves the gas, and then this solution is oxidized by the oxygen of the air to produce free sulphur and water.

$$\underset{\text{(in solution)}}{2\ H_2S} + \underset{\text{(air)}}{O_2} \longrightarrow 2\ H_2O + 2\ S$$

The free sulphur combines with the silver to form silver sulphide.

$$2\ Ag + S \longrightarrow Ag_2S$$

The tarnishing of copper and other metals can be explained in the same way.

(6) Hydrogen sulphide is a *very poisonous* substance, and even inhaling a small quantity of it produces headache and nausea.

5. The Chemical Test for a Sulphide

If a sulphide is soluble in water, it is only necessary to add a solution of lead acetate to it. The formation of a black precipitate of lead sulphide indicates the presence of the sulphide ion. For example, sodium sulphide, Na_2S, is a soluble sulphide and it reacts with lead acetate as follows:

$$\underset{\text{sodium sulphide}}{Na_2S} + \underset{\text{lead acetate}}{Pb\,(C_2H_3O_2)_2} \longrightarrow \underset{\text{lead sulphide}}{PbS}\downarrow + 2\ \underset{\text{sodium acetate}}{NaC_2H_3O_2}$$

In the case of an insoluble sulphide, such as zinc sulphide, add dilute hydrochloric acid to it. Then hold near the mouth of the test-tube a strip of paper which has been dipped in a lead acetate solution. The escaping gas (H_2S) is recognized by its odour and by the fact that it turns the paper black, due to the formation of black lead sulphide.

$$\underset{\text{zinc sulphide}}{ZnS} + 2\ HCl \longrightarrow H_2S\uparrow + ZnCl_2$$

$$Pb\,(C_2H_3O_2)_2 + H_2S \longrightarrow PbS\downarrow + 2\ HC_2H_3O_2$$

metallurgy

6. Uses

The chief use of hydrogen sulphide is in analytical chemistry. Most of the metallic sulphides are insoluble, and so they are precipitated when the gas is passed through solutions of their soluble salts. These sulphides have characteristic colours and this fact may be used in the laboratory as an aid to the identification of unknown metal ions.

$$ZnSO_4 + H_2S \longrightarrow \underset{\substack{\text{zinc sulphide}\\\text{(white)}}}{ZnS}\downarrow + H_2SO_4$$

$$CuSO_4 + H_2S \longrightarrow \underset{\substack{\text{cupric sulphide}\\\text{(black)}}}{CuS}\downarrow + H_2SO_4$$

$$2\ SbCl_3 + 3\ H_2S \longrightarrow \underset{\substack{\text{antimony}\\\text{sulphide}\\\text{(orange)}}}{Sb_2S_3}\downarrow + 6\ HCl$$

important

$$CdSO_4 + H_2S \longrightarrow \underset{\substack{\text{cadmium}\\\text{sulphide}\\\text{(canary yellow)}}}{CdS}\downarrow + H_2SO_4$$

$$2\ AgNO_3 + H_2S \longrightarrow \underset{\substack{\text{silver}\\\text{sulphide}\\\text{(black)}}}{Ag_2S}\downarrow + 2\ HNO_3$$

EXERCISES

1. Write a short note on the occurrence of hydrogen sulphide.
2. (a) Describe in detail the laboratory preparation of hydrogen sulphide.
   (b) Write the equation for the reaction in (a).
3. (a) Tabulate four physical properties of hydrogen sulphide.
   (b) Tabulate five chemical properties of the gas. Give one equation to illustrate each property.
4. Describe the chemical test for a sulphide.
5. (a) Why is hydrogen sulphide used in analytical chemistry?
   (b) The formula for arsenious chloride is $AsCl_3$. Write the equation for the reaction of this compound with H_2S.

CHAPTER XXXIII

SULPHUR DIOXIDE

1. Preparation

Sulphur dioxide usually occurs in the gases which escape from *volcanoes*. It is also present in the gases produced during the combustion of coal, which, as a rule, contains small amounts of sulphur, either in the free state or in the combined state. Sulphur dioxide is prepared by the following methods:

(1) COMMERCIAL.

(a) *By Burning Sulphur in Air.*

$$S + O_2 \longrightarrow SO_2$$

(b) *By Heating Metallic Sulphides in Air* (*roasting*).

$$\underset{\substack{\text{iron}\\\text{pyrites}}}{4\ FeS_2} + 11\ O_2 \longrightarrow \underset{\substack{\text{ferric}\\\text{oxide}}}{2\ Fe_2O_3} + 8\ SO_2\uparrow$$

$$\underset{\text{zinc blende}}{2\ ZnS} + 3\ O_2 \longrightarrow 2\ ZnO + 2\ SO_2\uparrow$$

Reactions similar to the above take place in the smelting (extraction of a metal from ore by heating) of many sulphide ores and so sulphur dioxide is likely to be present in the air near smelters. The gas destroys crops and this has caused much trouble between the companies which own smelters and the farmers nearby. In recent years most smelters have been forced either to install devices which collect the gas, or to allow it to escape in such small amounts that it is harmless to vegetation.

(2) LABORATORY.

(a) *Action of an Acid on a Sulphite.* Sulphur dioxide may be prepared on a small scale by the action of a *dilute* acid, such as hydrochloric or sulphuric, on either a sulphite or a bisulphite. For example, the gas is obtained by gently heating a mixture of sodium sulphite and dilute hydrochloric acid in an apparatus similar to that shown in Fig. 128.

$$\underset{\substack{\text{sodium}\\\text{sulphite}}}{Na_2SO_3} + 2\ HCl \longrightarrow 2\ NaCl + \underset{\substack{\text{sulphurous}\\\text{acid}}}{H_2SO_3}$$

$$H_2SO_3 \longrightarrow H_2O + SO_2\uparrow$$

If a bisulphite is used, the final reaction is:

$$NaHSO_3 + HCl \longrightarrow NaCl + H_2O + SO_2\uparrow$$

(b) *Heating Concentrated Sulphuric Acid with Copper.* Another laboratory method of preparing sulphur dioxide is to heat copper, in the form of turnings, with concentrated sulphuric acid (see Fig. 128).

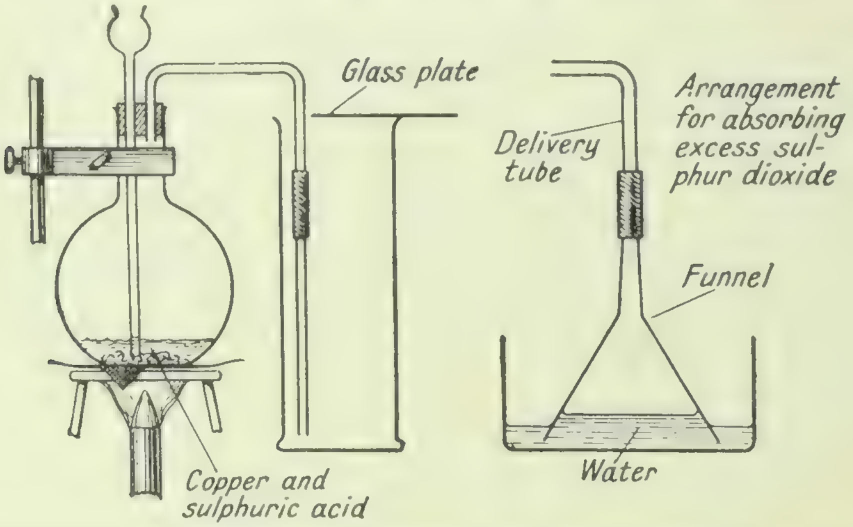

Glass plate
Delivery tube
Arrangement for absorbing excess sulphur dioxide
Funnel
Water
Copper and sulphuric acid

FIG. 128—A LABORATORY PREPARATION OF SULPHUR DIOXIDE

$$Cu + 2\ H_2SO_4 \longrightarrow CuSO_4 + 2\ H_2O + SO_2\uparrow$$

3. Physical Properties

(1) Sulphur dioxide is a *colourless gas.*
(2) It has a strong, choking odour (like that of burning matches).
(3) The gas is more than twice as heavy as air.
(4) Sulphur dioxide is very soluble in water.
(5) It can be easily liquefied to a colourless liquid at 20° C. by a pressure of slightly more than three atmospheres.

4. Chemical Properties

(1) Sulphur dioxide is a stable compound.
(2) The gas does not burn.
(3) It does not support combustion.
(4) Sulphur dioxide combines with water to form sulphurous acid. It is, therefore, an acid anhydride and the gas is often referred to as *sulphurous anhydride.*

$$H_2O + SO_2 \rightleftharpoons H_2SO_3$$

It is impossible to prepare pure sulphurous acid, as it breaks down very easily into water and sulphur dioxide. The reaction is, therefore, reversible and it is expressed by the above equation using double arrows.

Sulphurous acid is a typical acid. It turns blue litmus red, has a sour taste, and neutralizes bases, forming sulphites.

$$2\ NaOH + H_2SO_3 \longrightarrow \underset{\text{sodium sulphite}}{Na_2SO_3} + 2\ H_2O$$

$$Ca(OH)_2 + H_2SO_3 \longrightarrow CaSO_3 + H_2O$$

Some of these sulphites are used to convert wood into pulp, which is used in the manufacture of paper.

Sulphurous acid slowly takes up oxygen when in contact with the air, forming sulphuric acid.

$$2\ H_2SO_3 + O_2 \longrightarrow 2\ H_2SO_4$$

This process is, however, far too slow to be used as an industrial method for the production of sulphuric acid.

Sulphurous acid is a powerful *reducing agent* and this ability to remove oxygen from certain compounds can be illustrated by its action on hydrogen peroxide.

$$H_2SO_3 + H_2O_2 \longrightarrow H_2SO_4 + H_2O$$

Sulphurous acid also acts as a bleaching agent. If the dye in a material can be reduced by sulphurous acid, then a colourless substance can be secured. The reaction can be expressed as follows:

$$H_2SO_3 + \text{dye} \longrightarrow H_2SO_4 + \text{colourless compound}$$

Of course, the sulphuric acid must be removed from the cloth at once by washing with water.

5. A Chemical Test for Sulphurous Acid and for a Sulphite.

A test for sulphurous acid is to add it to a solution of potassium permanganate ($KMnO_4$). The permanganate solution has a reddish-purple colour, and on the addition of sulphurous acid it becomes colourless. In the reaction, the potassium permanganate is reduced and the sulphurous acid is oxidized to sulphuric acid.

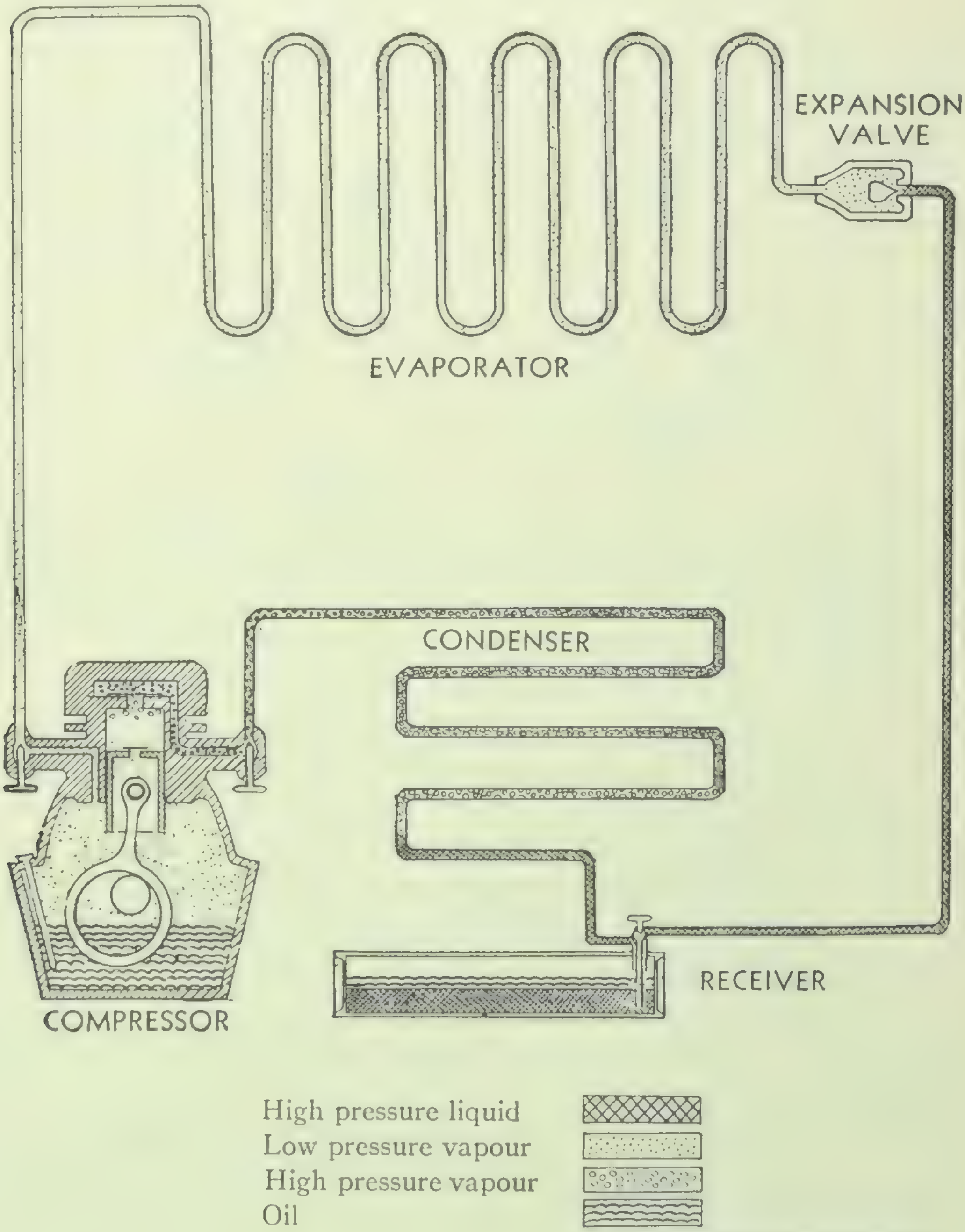
$$2\ KMnO_4 + 5\ H_2SO_3 \longrightarrow K_2SO_4 + 2\ MnSO_4 + 2\ H_2SO_4 + 3\ H_2O$$

To test for a sulphite, add some dilute hydrochloric acid to the unknown sample. If sulphur dioxide gas, which has the odour of burning sulphur, is produced, and if the gas decolourizes a solution of potassium permanganate, $KMnO_4$, then the original substance was a sulphite.

6. The Uses of Sulphur Dioxide

(1) FOR MAKING SULPHURIC ACID. This is by far the most important use of sulphur dioxide.

(2) For Bleaching. Moist sulphur dioxide is used to bleach wood pulp (for making paper), straw, wool, and silk. The gas is also used to bleach certain foods, such as canned corn and dried apples.



Courtesy of Beach Foundry.

Fig. 129—The Refrigeration Cycle

(3) For Refrigeration. Sulphur dioxide is easily liquefied and it is used to a considerable extent in domestic refrigeration units. It takes energy, in the form of heat, to bring about the evaporation of a liquid. When liquid sulphur dioxide evaporates in a refrigerator, it removes heat from the air inside the

food compartment, cooling it sufficiently to preserve food. The gaseous sulphur dioxide is converted back to the liquid state by means of the small compressor in the refrigerator, and the liquid is allowed to evaporate again. The process goes on continuously keeping the food chamber cool. A diagram of the process is shown in Fig. 129.

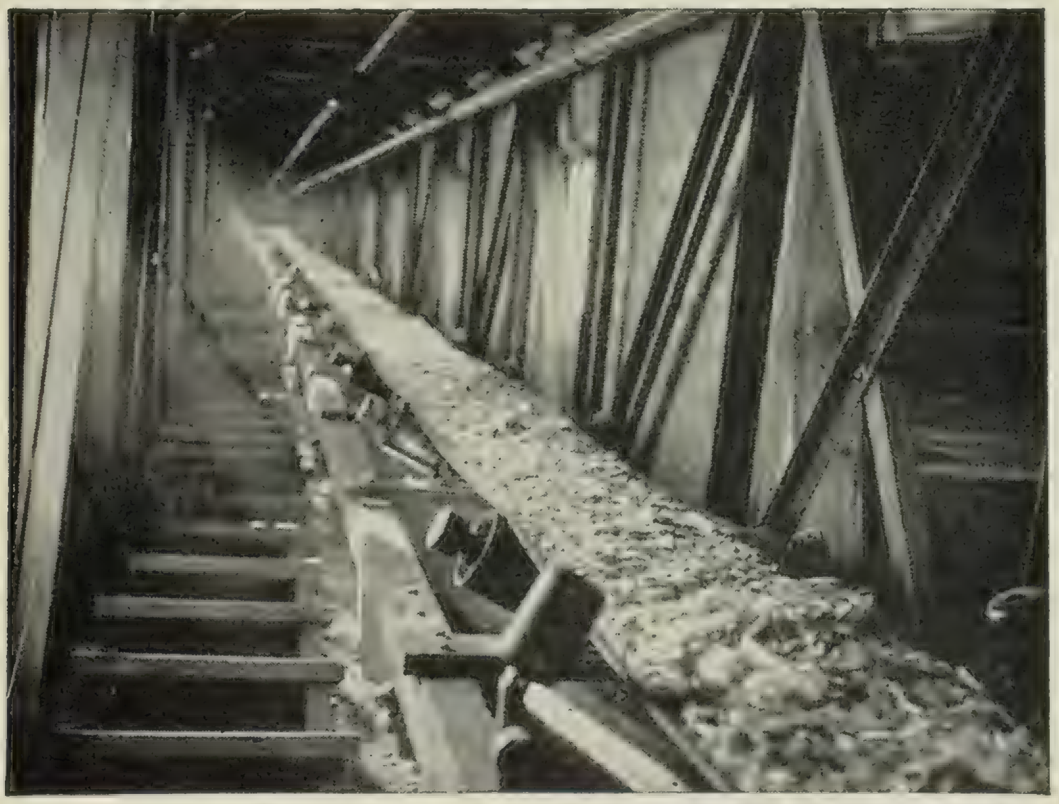
(4) FOR DISINFECTING. Sulphur candles are sometimes used to disinfect rooms which have been used by people with contagious diseases. Since the gas may corrode metal fixtures and bleach curtains and wall paper, its use for this purpose is somewhat limited.

(5) FOR MANUFACTURING SULPHITES. One sulphite, calcium acid sulphite, $Ca(HSO_3)_2$, is used in large quantities in the manufacture of *paper pulp* by the so-called sulphite process. This sulphite is produced by treating limestone, $CaCO_3$, suspended in water, with an excess of sulphurous acid.

$$H_2O + SO_2 \longrightarrow H_2SO_3$$

$$2\ H_2SO_3 + CaCO_3 \longrightarrow Ca(HSO_3)_2 + H_2O + CO_2\uparrow$$

Wood is composed chiefly of two substances, cellulose and lignin. Cellulose is the fibrous material needed to make paper, whereas



Courtesy of The E. B. Eddy Co. Ltd.

FIG. 130

These are wood chips in the first stage of the sulphite process.

the lignin is the gummy substance which holds the cellulose fibres together in the wood. To make a good grade of paper the lignin must be removed from the cellulose. This can be done by heating wood chips in huge digesters with a solution of calcium acid sulphite. Sulphurous acid is formed in the process and it dissolves the lignin. The cellulose, however, is unchanged by this treatment and it is then removed from the mixture by filtration.

Courtesy of The E. B. Eddy Co. Ltd.

FIG. 131

This is sulphite pulp obtained by heating wood chips in digesters with a solution of calcium acid sulphite. The pulp is washed free of the cooking solution before being used to make paper.

(6) FOR PRESERVING FOODS. Sulphur dioxide kills bacteria, and so tends to prevent fermentation. Since the gas may be injurious to human beings, such a method of preserving foods is of questionable value.

7. Comparison of Sulphur Dioxide and Carbon Dioxide

(1) Sulphur dioxide and carbon dioxide are both oxides of non-metals.

(2) The two gases are both acid anhydrides, forming weak and unstable acids with water.

$$SO_2 + H_2O \longrightarrow \underset{\text{sulphurous acid}}{H_2SO_3}$$

$$CO_2 + H_2O \longrightarrow \underset{\text{carbonic acid}}{H_2CO_3}$$

(3) They do not burn.
(4) The two gases do not support combustion.
(5) These two compounds are both colourless gases.

EXERCISES

1. Write a note on the occurrence of sulphur dioxide.
2. Discuss briefly the commercial methods of preparing sulphur dioxide. Use equations in your answer.
3. (a) Describe briefly the laboratory method of preparing sulphur dioxide from sodium sulphite and hydrochloric acid. Illustrate your answer with a labelled diagram.
   (b) Write the equation for the reaction in (a).
   (c) Write the equation for the preparation of sulphur dioxide by the action of concentrated sulphuric acid on copper.
4. (a) Tabulate *five* physical properties of sulphur dioxide.
   (b) Tabulate *four* chemical properties of the gas.
   (c) Tabulate five uses of sulphur dioxide.
5. (a) How is sulphurous acid prepared?
   (b) Can the acid be prepared in the pure state? Explain.
   (c) What is a reversible reaction? Illustrate by an equation.
6. (a) What are sulphites?
   (b) Write the equations for the preparation of sodium sulphite and calcium sulphite.
   (c) Discuss the use of sulphurous acid in the pulp and paper industry.
7. (a) What is a reducing agent?
   (b) Is sulphurous acid a reducing agent?
   (c) Discuss carefully the bleaching action of sulphur dioxide.
8. What weight of sodium sulphite is needed to produce 10 litres of sulphur dioxide at S.T.P.?

CHAPTER XXXIV

SULPHURIC ACID

1. History and Importance of Sulphuric Acid

Impure forms of sulphuric acid have been known for many years. It was one of the most important reagents used by the alchemists, the pioneer chemists. In the fifteenth century the acid was made by distilling ferrous sulphate, $FeSO_4$, with sand in a galley furnace, the acid being collected in receivers along the side of the furnace, as shown in Fig. 132 (see foot-note). This method was, however, very inefficient, and the product contained much water and sulphur dioxide. The problem of making the acid stronger by some less costly process grew in importance as the demands of industry developed. In 1831, P. Phillips, an English chemist, patented a process in which the gas from burning sulphur was passed with air over hot platinum, and the sulphur trioxide, SO_3, so produced dissolved in water to give acid of any required strength. This process, simple as it sounds, presented great difficulties, but when the needs of the synthetic dyestuff industry, founded in 1870, were added to those of other industries, the demand for cheap fuming acid became so great that the technical problems had to be overcome. Before the century was

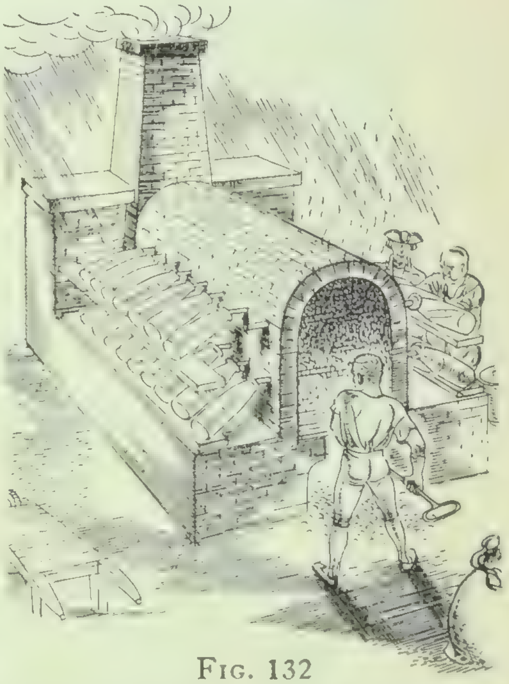


FIG. 132

Acid of "indescribable strength," or oleum as it is now called, was probably one of the earliest varieties of sulphuric acid produced for sale. Green vitriol was heated in a galley furnace similar to that shown in the above illustration and the acid collected in receivers attached along the side of the furnace.

The equations for the reactions involved in the preparation of sulphuric acid by the distillation of ferrous sulphate are:

$$\underset{\text{ferrous sulphate (green vitriol)}}{2\,FeSO_4 \cdot 7\,H_2O} \longrightarrow Fe_2O_3 + SO_2 + SO_3 + 7\,H_2O$$

$$SO_3 + H_2O \longrightarrow \underset{\text{(oil of vitriol)}}{H_2SO_4}$$

out, acid of all strengths was being cheaply produced by the contact process, which was essentially the one patented by Phillips.

When a chemist thinks of the chemical industries he usually places sulphuric acid first. Enormous quantities of it are used in commerce, and it would be hard to name any one chemical compound of more fundamental importance in the industrial life of a nation. Sulphuric acid is as important in the chemical industries as steel is in the mechanical and construction industries.

2. Preparation

Two general methods for the manufacture of sulphuric acid are in use at the present time. The newer one of these is known as the *contact* process, while the older one is called the *lead chamber* process.

In both processes the reactions which take place may be represented as follows:

$$S + O_2 \longrightarrow SO_2$$

$$2\ SO_2 + O_2 + \text{catalyst} \longrightarrow 2\ SO_3$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

The chief difference between the two methods is in the catalyst used. In the lead chamber process the catalyst consists of a mixture of *gases*, nitric oxide, NO, and nitrogen dioxide, NO_2. In the contact process the catalyst is a *solid*, finely divided platinum, or certain complex vanadium compounds containing pentavalent vanadium. *Contact acid* is highly concentrated (about 98%), while *chamber acid* is relatively dilute (60 to 70%).

THE CHAMBER PROCESS. Sulphur is one of the chief raw materials of this process. It is shipped from Texas by ship and railroad and unloaded at the plant onto a huge pile. The sulphur is carried from the pile to a large furnace where it is burned, producing sulphur dioxide gas, SO_2. The gas is then piped to a series of huge lead chambers (see Fig. 133). Lead is used because it is almost the only metal which the acid will not attack. As the sulphur dioxide enters the chamber it meets a mixture of nitrous fumes (NO and NO_2), air, and steam (or a fine spray of water). The sulphur dioxide, under the influence of the gaseous catalyst, combines with the oxygen of the air to produce sulphur trioxide, SO_3. This compound combines with water to form sulphuric acid, H_2SO_4, which falls to the bottom of the chamber as shown in Fig. 133. The technical details of the process and the chemical reactions which take place are quite complex and cannot be considered in this text. Fig. 133 attempts to show this process in diagrammatic form.

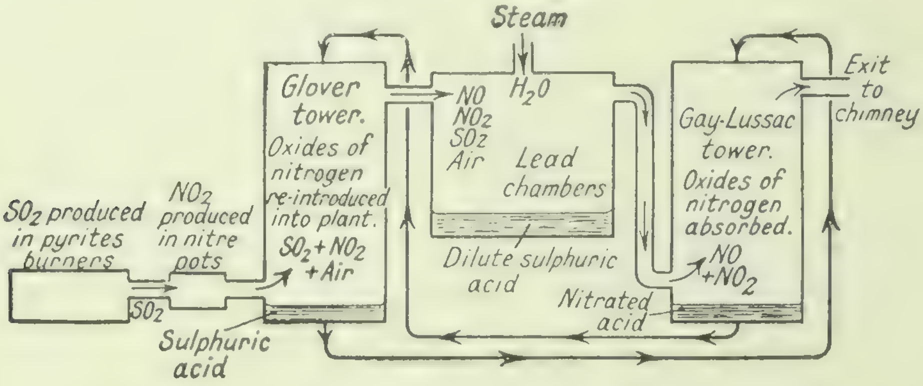

Steam
Glover tower. Oxides of nitrogen re-introduced into plant.
SO_2 + NO_2 + Air
NO
NO_2
SO_2
Air
H_2O
Lead chambers
Dilute sulphuric acid
Gay-Lussac tower. Oxides of nitrogen absorbed.
Exit to chimney
NO + NO_2
Nitrated acid
SO_2 produced in pyrites burners
NO_2 produced in nitre pots
SO_2
Sulphuric acid

Fig. 133—The Manufacture of Sulphuric Acid by the Chamber Process

The Contact Process. Fig. 134 attempts to represent this process in diagrammatic form. The chief steps in the process are as follows:

(1) *Production of Sulphur Dioxide.* Sulphur dioxide is produced by burning sulphur or by roasting of metallic sulphides.

$$S + O_2 \longrightarrow SO_2$$
$$2\ ZnS + 3\ O_2 \longrightarrow 2\ ZnO + 2\ SO_2$$

The gas is then mixed with an excess of air.

(2) *Purification of Sulphur Dioxide and Air.* This part of the process is very important since the sulphur dioxide and air must be free of dust particles, moisture, and other impurities to prevent the catalyst from becoming "poisoned" and so made inactive. This is done by passing the mixture of sulphur dioxide and air through a number of towers which remove the dust, moisture, and other impurities in various ways.

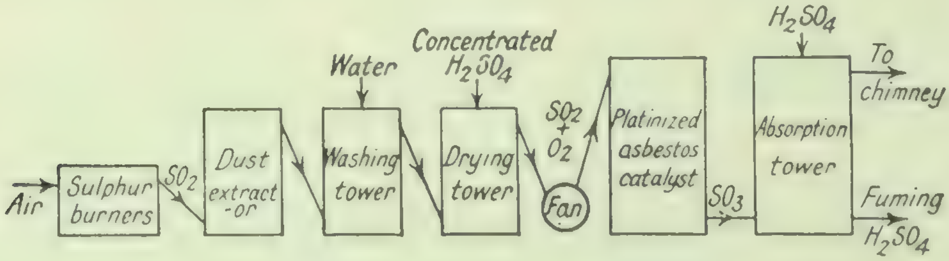


Fig. 134—The Manufacture of Sulphuric Acid by the Contact Process

(3) *Formation of Sulphur Trioxide.* The cleansed mixture of sulphur dioxide and air is preheated and passed through towers called *converters*. These contain the catalyst (called the contact agent) which is usually finely divided platinum (deposited on the surface of some inert material such as magnesium sulphate, asbestos, or silica gel), or complex vanadium compounds containing pentavalent vanadium. The best temperature in the contact process has been found to be between 425° C. and 450° C. The reaction which takes place in the converters is a reversible one and it is expressed as follows:

$$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3$$

(4) *Formation of Fuming Sulphuric Acid.* The products from the converters are cooled and then passed through towers filled with some inert material, such as quartz, down which concentrated sulphuric acid (98%) is pumped. The sulphur trioxide combines with the concentrated sulphuric acid to form *oleum* or *fuming sulphuric acid.*

$$SO_3 + H_2SO_4 \longrightarrow \underset{\text{oleum}}{H_2SO_4.SO_3}$$

It has been found that this method of absorbing the sulphur trioxide is more efficient than passing it into water. The fuming sulphuric acid is then diluted with the correct amount of water, forming concentrated sulphuric acid.

$$H_2SO_4.SO_3 + H_2O \longrightarrow 2\ H_2SO_4$$

The contact process has several distinct advantages as compared to the lead chamber process. The acid produced by the contact process is very pure, whereas the acid from a lead chamber plant contains some impurities. The contact process produces any concentration of sulphuric acid from oleum to a very dilute solution. The contact process is much more compact and so requires less space than the chamber method.

The preparation of sulphur trioxide in the laboratory may be accomplished as shown below in Fig. 135.

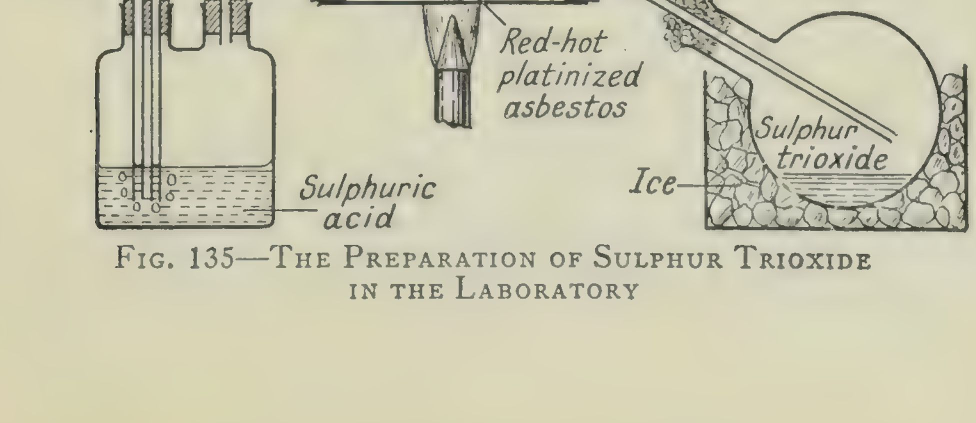


FIG. 135—THE PREPARATION OF SULPHUR TRIOXIDE IN THE LABORATORY

3. Physical Properties of Sulphuric Acid

(1) Concentrated sulphuric acid is a *colourless, syrupy, corrosive liquid* which is often called *oil of vitriol.*

(2) It is *odourless.*

(3) The concentrated acid is nearly *twice as heavy as water,* having a specific gravity of 1.84.

(4) Sulphuric acid is *soluble in water in all proportions.*

(5) It boils at 338° C. and so it is the *least volatile of all ordinary acids.*

4. Chemical Properties.

(1) STABILITY. Sulphuric acid is very stable at ordinary temperatures but, when it is heated, sulphur trioxide, in white fumes, starts to escape far below the boiling point of the liquid.

$$H_2SO_4 + \text{Heat} \longrightarrow H_2O + SO_3\uparrow$$

The sulphur trioxide and water combine in the cool air above the dish to form a dense white fog, consisting of fine droplets of sulphuric acid.

(2) AN ACID. A water solution of sulphuric acid has all the properties of a typical acid. A dilute solution of the acid ionizes as follows:

$$H_2SO_4 \rightleftharpoons 2\ H^+ + SO_4^{--}$$

The presence of hydrogen ions is shown by the fact that a solution of the acid turns blue litmus red. Dilute solutions of sulphuric acid react with metals, above hydrogen in the electromotive series, liberating hydrogen.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$$

It also reacts with oxides to form salts. For example, copper sulphate, $CuSO_4$, is produced when cupric oxide, CuO, is treated with sulphuric acid.

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

The acid also neutralizes bases.

$$2\ KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2\ H_2O$$

Dilute sulphuric is a strong acid and liberates weaker acids from their salts. For example, H_2S is liberated from sulphides, and H_2SO_3 from sulphites.

$$FeS + H_2SO_4 \longrightarrow H_2S\uparrow + FeSO_4$$
$$Na_2SO_3 + H_2SO_4 \longrightarrow H_2SO_3 + Na_2SO_4$$

(3) ACTION ON WATER. Much heat is given off when sulphuric acid is added to water and this fact suggests that some

chemical change takes place. Chemists are not certain as to what the reaction is, but it is likely that the acid forms hydrates. Whatever the action may be, the water is combined quite firmly. This fact makes concentrated sulphuric acid a good drying agent when moist gases are bubbled through it. The heat given off by the combination of the acid with the water makes the mixing of the two liquids dangerous, if it is not done correctly. *The concentrated sulphuric acid, being heavier, should be added to the lighter water slowly with constant stirring.* This method brings about complete mixing at once and the heat of the reaction is absorbed by the whole body of the fluid. If the opposite method is used, the water is likely to float on the acid. The heat produced is held to the area between the two liquids, and it becomes so great at that point that the water rapidly changes into steam, which throws out the very corrosive contents of the vessel with almost explosive violence.

(4) DEHYDRATING ACTION. Concentrated sulphuric acid has so strong an affinity for water that it often removes the elements of water (hydrogen and oxygen) from compounds containing them. This effect is especially marked if the compounds contain the elements in the same proportion as in water. For example, wood, paper, and sugar are charred by concentrated sulphuric acid because of the removal of hydrogen and oxygen, leaving a black residue which is chiefly carbon. The action is known as *dehydration.*

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + \underset{\substack{\text{concentrated}\\\text{sulphuric acid}}}{H_2SO_4} \longrightarrow (H_2SO_4 + 11\ H_2O) + 12\ C$$

(5) OXIDIZING AGENT. Concentrated sulphuric acid is an active oxidizing agent when heated. For example, the hot acid reacts with metals as an oxidizing agent, usually liberating sulphur dioxide.

$$\begin{array}{l}
(1)\ H_2SO_4 + Cu \longrightarrow \cancel{H_2SO_3} + \cancel{CuO} \\
(2)\ \cancel{CuO} + H_2SO_4 \longrightarrow CuSO_4 + H_2O \\
(3)\ \cancel{H_2SO_3} \longrightarrow H_2O + SO_2 \\
\hline
(4)\ 2\ H_2SO_4 + Cu \longrightarrow CuSO_4 + 2\ H_2O + SO_2\uparrow
\end{array}$$

The above equations can be used to explain the oxidation of copper by hot concentrated sulphuric acid. Equations (1), (2), and (3) represent the steps of the reaction, and (4) represents the final result.

(6) Action Due to Low Volatility. Concentrated sulphuric acid reacts with many salts, forming volatile acids. This is the basis for the preparation of most of the common acids. For example, when it is added to common salt, hydrogen chloride is driven off as a gas.

$$2\ NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ HCl \uparrow$$

Nitric acid can also be made by the same method.

$$2\ NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ HNO_3 \uparrow$$

Concentrated sulphuric acid is used in the above reactions because of its low volatility. Its boiling point is 338° C., which is considerably higher than that of most common acids.

5. The Chemical Test for Sulphuric Acid and for Sulphate Ions

$$H_2SO_4 \rightleftharpoons 2\ H^+ + SO_4^{--}$$

From the above equation it is clear that a solution of sulphuric acid contains two different ions, the hydrogen ion (H^+) and the sulphate ion (SO_4^{--}). The presence of the hydrogen ion is indicated by the fact that a dilute solution of sulphuric acid turns blue litmus red. The presence of the sulphate ion is shown by adding a solution of barium chloride ($BaCl_2$) to the acid. A white precipitate, barium sulphate ($BaSO_4$), insoluble in hydrochloric acid, is formed. This test applies to all soluble sulphates.

$$H_2SO_4 + \underset{\text{barium chloride}}{BaCl_2} \longrightarrow \underset{\text{barium sulphate}}{BaSO_4} \downarrow + 2\ HCl$$

$$\underset{\text{magnesium sulphate}}{MgSO_4} + BaCl_2 \longrightarrow \underset{\text{barium sulphate}}{BaSO_4} \downarrow + 2\ MgCl_2$$

6. Uses of Sulphuric Acid

(1) In the Manufacture of Fertilizers. The fertilizer industry has used sulphuric acid for many years for the production of soluble *super-phosphate* from insoluble phosphate rock (calcium phosphates).

(2) In the Refining of Petroleum. The acid is used to remove certain undesirable substances from petroleum products.

(3) In the Manufacture of Other Acids. It is used to a considerable extent in the manufacture of other acids, such as hydrochloric acid and nitric acid.

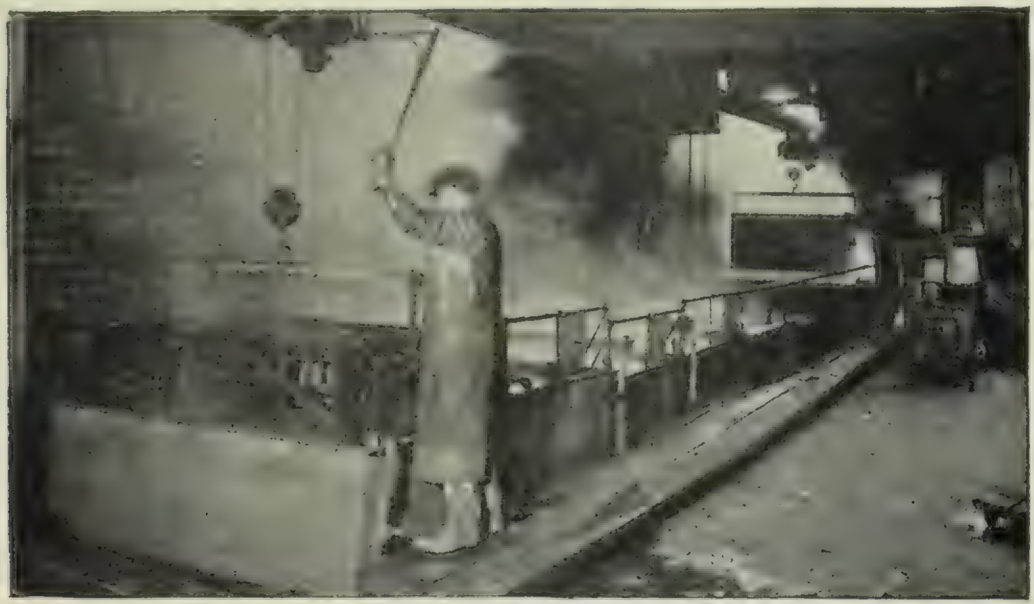
(4) Pickling of Steel. Before steel is coated with enamel, tin, or zinc (galvanized), the surface is cleaned of iron rust (iron

oxide) by dipping the metal into a "pickling bath" of sulphuric acid as shown in Fig. 136.

(5) STORAGE BATTERIES. All lead storage batteries contain sulphuric acid and thousands of tons are used every year for this purpose.

(6) IN THE MANUFACTURE OF RAYON. Much sulphuric acid is used in the production of rayon from wood pulp.

(7) IN THE MANUFACTURE OF EXPLOSIVES. Nearly every explosive requires sulphuric acid in the process of production.



Courtesy of International Nickel Co. of Canada Ltd

FIG. 136

This shows pickling baths containing hot dilute sulphuric acid. Steel is dipped in the acid for a short time to remove rust before being given a protective coating of enamel, tin, or zinc.

7. The Basicity of Acids

The term *basicity* refers to the number of replaceable hydrogen atoms obtainable from one molecule of an acid. Hydrochloric acid (HCl) is a *monobasic* acid since it has only one replaceable hydrogen atom in its molecule. Sulphuric acid (H_2SO_4) is a *dibasic* acid because its molecule contains two replaceable hydrogen atoms. Phosphoric acid (H_3PO_4) is a *tribasic* acid because its molecule has three replaceable hydrogen atoms. It is important to remember that the basicity of an acid is the number of *replaceable hydrogen atoms* and it is not always the total number of hydrogen atoms in the molecule. For example, acetic acid ($HC_2H_3O_2$) has four hydrogen atoms in its molecule, yet it is a monobasic acid because only one of these hydrogen atoms is replaceable by a metal.

When all the replaceable hydrogen atoms in the molecule of an acid have been replaced, the product is known as a *normal salt*. For example, sodium sulphate, Na_2SO_4, is a normal salt of sulphuric acid. Sodium phosphate, Na_3PO_4, is a normal salt of phosphoric acid.

When only a part of the hydrogen atoms in the molecule of an acid have been replaced, the product is called an *acid salt*. Sodium hydrogen sulphate or sodium bisulphate, $NaHSO_4$, is a good example of an acid salt. Sodium hydrogen carbonate, also known as sodium bicarbonate or baking soda, $NaHCO_3$, is another good example of an acid salt.

EXERCISES

1. Write a note on the history and importance of sulphuric acid.
2. (a) What are the commercial methods of preparing sulphuric acid?
   (b) Write the chemical equations for the reactions which take place in both processes.
   (c) What are the essential differences between the two processes?
3. Write a brief note on the lead chamber process.
4. Describe the contact process in detail. Give a simple sketch of a contact plant.
5. (a) Tabulate five physical properties of sulphuric acid.
   (b) Tabulate five chemical properties of the acid, illustrating with equations whenever possible.
6. What chemical tests would you do to show that an unknown liquid was sulphuric acid?
7. Tabulate five important industrial uses of sulphuric acid.
8. (a) What is meant by the term basicity of acids?
   (b) What is a normal salt? Give two examples.
   (c) What is an acid salt? Give two examples.

CHAPTER XXXV

THE THEORY OF IONIZATION

1. The Observed Facts

The Ionic Theory, often called the *Theory of Electrolytic Dissociation*, was proposed in 1887 by Svante Arrhenius, a great Swedish chemist, to explain certain *observed facts* concerning *solutions*. These facts were obtained as follows:

(1) FROM A STUDY OF ELECTRICAL CONDUCTION IN SOLUTIONS. Early in his series of great discoveries about electric currents, Michael Faraday, one of the greatest experimenters of all time, became interested in the problem of how an electric current passes through a solution. He knew that pure water has almost no power to conduct an electric current, but if the water has dissolved in it certain substances, such as common salt or sulphuric acid, it becomes a good conductor. Faraday gave the name of *electrolytes* to those substances which, in solution, conduct the electric current. It can be shown by experiment (see Fig. 137) that solutions of acids, bases and salts conduct the electric current; that is, they are electrolytes. Substances which do not conduct the electric current, when dissolved in water, are known as non-electrolytes. Sugar, alcohol, glycerine, and carbon tetrachloride, are examples of non-electrolytes.

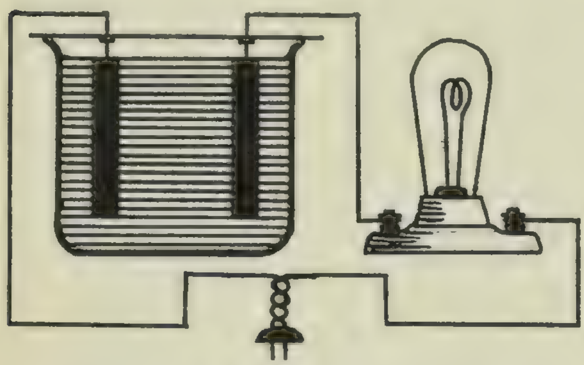


FIG. 137—AN APPARATUS FOR TESTING THE CONDUCTIVITY OF SOLUTIONS

(2) FROM A STUDY OF ELECTROLYSIS. Electrolysis is the decomposition of a substance by electricity. For example, a concentrated solution of hydrochloric acid can be decomposed by electricity into hydrogen and chlorine. The hydrogen bubbles off around the negative electrode, which is known as the cathode, and the chlorine comes off at the positive electrode, known as the anode. This is shown in Fig. 138.

$$2\,\mathbf{HCl} + \textbf{Direct Current} \longrightarrow \mathbf{H_2}\uparrow + \mathbf{Cl_2}\uparrow$$

Experiments have shown that only solutions of acids, bases, and salts can be decomposed by electrolysis. Other substances in solution cannot be decomposed by electricity.

(3) FROM A STUDY OF DOUBLE DECOMPOSITION REACTIONS (Metathesis). The reaction between silver nitrate and sodium chloride is a good illustration of a double decomposition reaction.

$$\mathbf{NaCl + AgNO_3 \longrightarrow AgCl\downarrow + NaNO_3}$$

The neutralization of sodium hydroxide by hydrochloric acid is another example of this type of reaction.

$$\mathbf{NaOH + HCl \longrightarrow NaCl + H_2O}$$

From a consideration of the above examples, it is evident that a double decomposition reaction is simply an exchange of partners. For the most part, only acids, bases, and salts react in this way, whereas other substances in solution do not react in this manner.

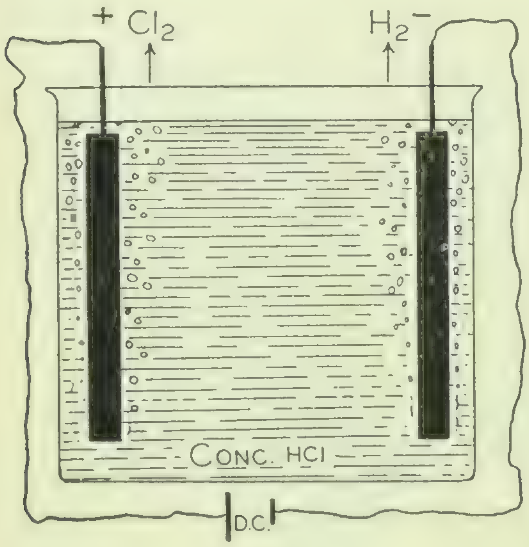


FIG. 138
ELECTROLYSIS OF A CONCENTRATED HYDROCHLORIC ACID SOLUTION

(4) FROM A STUDY OF THE SPEED OF REACTIONS. The speed of a reaction is defined as the quantity of reacting substances changed into other materials per unit of time. Solutions of acids, bases, and salts, are very active; they react with each other almost at once. Other substances in solution, however, react slowly.

(5) FROM A STUDY OF THE EFFECT OF SOLUTES ON THE BOILING AND FREEZING POINTS OF PURE SOLVENTS. In the chapter on solutions it was found that solutes have a marked effect on the boiling and freezing points of a solvent. When the solvent is water, it is found that the gram molecular weight of a substance dissolved in 1000 grams of water raises the boiling point exactly 0.52°C. Ten gram molecular weights of the substance, dissolved in the same weight of water, elevates the boiling point exactly 5.2° C. Since there are ten times as many molecules of the substance in ten gram molecular weights as in one molecular weight, it is evident that the elevation of the boiling point must be directly proportional to the number of molecules (particles) of solute present in the solution. In the

case of the freezing point, it is found that one gram molecular weight of a substance dissolved in 1000 grams of water, lowers the freezing point exactly 1.86°C. Ten gram molecular weights dissolved in the same weight of water lowers the freezing point 18.6°C. Thus, it is also evident that the depression of the freezing point is directly proportional to the number of dissolved molecules (particles). Solutions of acids, bases, and salts, however, give *abnormal values* for boiling point elevation and freezing point depression. For example, a gram molecular weight of sodium chloride (common salt) dissolved in 1000 grams of water raises the boiling point almost twice 0.52°C., and it lowers the freezing point almost twice 1.86°C. These facts suggest that a solution of sodium chloride must contain more dissolved particles than normal substances. This abnormal behaviour of acids, bases, and salts suggests that the molecules of these substances must break up some way to produce more particles when they are in solution.

2. Arrhenius's Theory of Ionization

The above observed facts regarding solutions were explained by a theory of *electrolytic dissociation* or of *ionization*, which was developed by Svante Arrhenius, an outstanding Swedish chemist, in 1887. This theory is also known as the *Ionic* theory.

The chief assumptions of the theory are:

(1) DISSOCIATION INTO ELECTRICALLY CHARGED PARTICLES CALLED IONS. When an acid, base, or salt, is dissolved in water, its molecules are at once, more or less completely, *dissociated by the water* into smaller particles of unlike composition, called ions. This process is known as *ionization* or *electrolytic dissociation.* Substances, such as acids, bases, and salts, which ionize in water, are called *ionogens.* To express this idea, Arrhenius proposed the use of *ionic equations*, a few of which are shown below.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$HCl \rightleftharpoons H^+ + Cl^-$$

$$H_2SO_4 \rightleftharpoons 2\ H^+ + SO_4^{--}$$

$$BaCl_2 \rightleftharpoons Ba^{++} + 2\ Cl^-$$

$$MgSO_4 \rightleftharpoons Mg^{++} + SO_4^{--}$$

$$AlCl_3 \rightleftharpoons Al^{+++} + 3\ Cl^-$$

From a study of the above equations it is evident that hydrogen and the metal ions are *positively charged*, and the non-metal and acid radicals are *negatively charged.* It is important to observe that the charge on any ion is always the same as its valence.

(2) THE WHOLE SOLUTION IS ELECTRICALLY NEUTRAL. The unit positive charge on an ion is equal in quantity, but opposite in kind, to the unit negative charge. *The sum of all the positive charges in a solution is equal to the sum of all the negative charges*, and so the whole solution is electrically neutral.

(3) *Ionization is a Reversible Reaction.* The dissociation into ions is a *reversible* reaction, and this is indicated in all ionic equations by means of double arrows.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Addition of more water to a solution of an electrolyte increases its ionization and, when a great deal of water has been added, the electrolyte is considered to be *completely ionized.* This is said to be at *infinite dilution.* Evaporation of water from a solution of an electrolyte gives the ions less room in which to move, and so the chances of combining together again to form molecules are greater. If all the water is driven off, the ions are completely changed back into crystals or molecules.

(4) *Ions Possess Specific Properties.* Except for the dependence due to their electrical charges and the resulting attractions and repulsions between ions, the ions must be considered independent particles with their own *specific chemical* and *physical* properties. For example, some ions possess a definite colour, whereas others are colourless. A water solution of sulphuric acid is colourless.

$$H_2SO_4 \rightleftharpoons 2\ H^+ + SO_4^{--}$$

According to the ionic theory a dilute water solution of sulphuric acid ionizes into hydrogen (H^+) and sulphate (SO_4^{--}) ions as shown by the above equation. Thus, it is evident that hydrogen and sulphate ions are both colourless. A water solution of copper sulphate, on the other hand, is blue in colour.

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$

This salt ionizes in solution according to the above equation. Since the sulphate ion is colourless, the blue colour of the copper sulphate solution must be due to the copper ion (Cu^{++}). The colour of other ions could be determined by the same method.

The velocity at which ions move through a solution, under the influence of an electrical force, is another example of a specific property of ions. For example, hydrogen ions move much faster than copper ions, under the influence of the same electrical force. Other specific properties will be considered in the next chapter.

3. How Does the Theory of Ionization Explain the Observed Facts Concerning Solutions?

A theory is proposed in science to explain certain facts or laws. The Theory of Ionization was proposed by Arrhenius to explain certain peculiar facts, which had been observed concerning solutions. Let us now consider how this theory explains these facts.

(1) Electrical Conductance by Electrolytes. When a current is passed through a solution of an electrolyte (acid, base, or salt), the ions (charged particles) carry their charges to the electrodes. It is interesting to know that the word *ion* is derived from the Greek and means "the going or the migrating particle." The positively charged ions go to the *cathode* (negative electrode) and they are known as *cations*. The negatively charged ions move to the *anode* (positive electrode) and they are called *anions*. In the case of a solution of hydrochloric acid, the negative charge on the cathode would attract the hydrogen ions and repel the chloride ions. On the other hand, the positive charge of the anode would attract the chloride ions and repel the hydrogen ions. The net result would be a migration of all the chloride ions with their negative charges toward the anode (positive), and of the positively charged hydrogen ions toward the cathode. In this way a flow or *current of electricity* is produced. The fact, then, that a current of electricity does readily pass through solutions of acids, bases, and salts, is easily understood on the basis of the ionic theory.

(2) Electrolysis. According to the Ionic theory, acids, bases, and salts dissociate, when placed in water or some other suitable solvent, into electrically charged particles (ions). When ions touch an electrode, they are discharged, and with the discharge, are changed *chemically*. For example, when a current is passed through a solution of hydrochloric acid, the hydrogen ions (H^+) are attracted

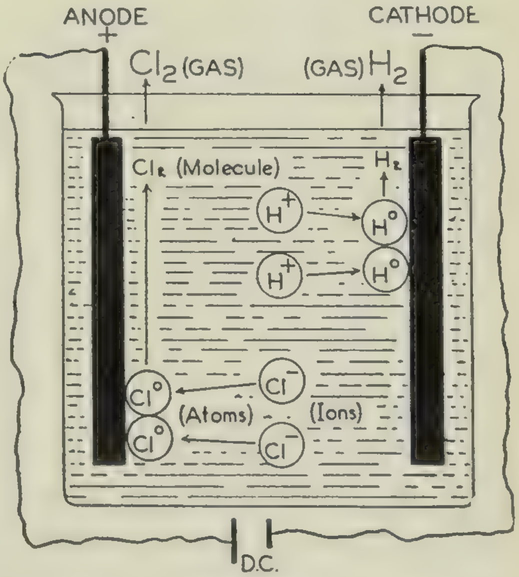


Fig. 139—Explanation of the Electrolysis of Hydrochloric Acid by Means of the Ionic Theory

to the cathode (negative) where they are discharged. Two of these discharged ions share a pair of electrons to form a hydrogen molecule. Millions of such molecules form bubbles of hydrogen gas. The chloride ions (Cl^-) are attracted to the anode (positive) where they are discharged. Two of these discharged ions share a pair of electrons to form a chlorine molecule and millions of these form bubbles of chlorine gas. A diagram representing the electrolysis of hydrochloric acid is shown in Fig. 139. Equations for the reactions at the electrodes are shown below.

At cathode

$$\underset{\text{(hydrogen ion)}}{H^+} + 1 \text{ electron} \longrightarrow \underset{\text{(hydrogen atom)}}{H^\circ}$$

$$H^\circ + H^\circ \xrightarrow[\text{of electrons}]{\text{share 1 pair}} \underset{\text{(gas molecule)}}{H_2}$$

At anode

$$\underset{\text{(chlorine ion)}}{Cl^-} - 1 \text{ electron} \longrightarrow \underset{\text{(chlorine atom)}}{Cl^\circ}$$

$$Cl^\circ + Cl^\circ \xrightarrow[\text{of electrons}]{\text{share 1 pair}} \underset{\text{(gas molecule)}}{Cl_2}$$

(3) Double Decomposition Reactions. Experiments have shown that most double decomposition reactions are those between electrolytes. Up to the present time a reaction between two electrolytes, such as that between sodium chloride ($NaCl$) and silver nitrate ($AgNO_3$), has been expressed by a molecular equation as follows:

$$NaCl + AgNO_3 \longrightarrow AgCl\downarrow + NaNO_3$$

According to the Ionic theory this reaction should be expressed as follows:

$$\begin{array}{rcl} NaCl & \rightleftharpoons & Na^+ + Cl^- \\ AgNO_3 & \rightleftharpoons & NO_3^- \;+\; Ag^+ \\ & & \quad\upharpoonleft\!\downharpoonright \qquad\ \downarrow \\ & & \underset{\text{(soluble)}}{NaNO_3}\ \ \underset{\text{(insoluble)}}{AgCl} \end{array}$$

The above equations are known as ionic equations. They show that the reaction between two electrolytes really consists of reactions between their ions and not between the molecules themselves. Thus, the silver ion (Ag^+) combines with the chloride ion (Cl^-) to form silver chloride ($AgCl$), which is insoluble in water, and so it cannot dissociate into ions. The sodium ions

(Na^+) combine with the nitrate ions (NO_3^-) to form sodium nitrate ($NaNO_3$), which is very soluble and highly ionized, and so it dissociates at once into its ions. Other examples could be given to show that the double decomposition reactions of acids, bases, and salts can be explained satisfactorily by means of the theory of ionization.

(4) THE SPEED OF REACTIONS. From the above discussion it was found that the reactions between electrolytes are due to their ions. The ions are formed as soon as the electrolyte is dissolved in water, and so when two ionogens are mixed the ions of opposite charge combine at once. The time of reaction is regulated by the speed of mixing. Thus, the idea of ions explains the marked activity of solutions of acids, bases, and salts.

(5) THE EFFECT OF SOLUTES ON THE BOILING AND FREEZING POINTS OF PURE SOLVENTS. It has been shown that the presence of a solute elevates the boiling point and lowers the freezing point of a pure solvent. Furthermore, these effects are directly proportional to the number of dissolved molecules or particles. According to the Ionic theory, acids, bases, and salts dissociate more or less completely into smaller fragments, known as ions. These dissociation products act in solution as individual particles and elevate the boiling point or depress the freezing point of a solvent in the same way as any other dissolved molecules do. For example, sodium chloride in water ionizes almost completely as follows:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

and so a gram molecular weight of this substance, dissolved in 1000 grams of water, would contain almost twice as many particles as the gram molecular weight of a non-electrolyte, such as cane sugar. It would, therefore, be expected that the boiling point of water would be elevated almost twice 0.52°C. when one gram molecular weight of sodium chloride is dissolved in 1000 grams of water. Experiments show that such is the case. Thus, the theory of ionization is able to explain the abnormal elevation of the boiling point and abnormal depression of the freezing point caused by dissolving electrolytes in water or other solvents.

EXERCISES

1. Tabulate the chief points of the Theory of Ionization.
2. Show clearly how the Ionic theory explains the conducton of an electric current by a solution of copper chloride.

3. Show how the Ionic theory explains the electrolysis of a concentrated solution of hydrochloric acid. Use a labelled diagram to illustrate your answer, and use equations to explain the reactions at each electrode.

4. Write ionic equations for the following reactions:
   (a) Barium chloride and sodium sulphate.
   (b) Silver nitrate and hydrochloric acid.

5. Explain carefully why a solution of potassium chloride produces an abnormal effect on the freezing point and the boiling point of water.

CHAPTER XXXVI

APPLICATIONS OF THE IONIC THEORY

1. Applications to Acids

Before studying the theory of ionization, an acid was considered to be a substance which, in solution, turned blue litmus red. Now we can define an acid as *a compound which gives hydrogen ions in solution and no other positively charged ions.* The equations for the ionization of a few acids are given below:

$$\mathbf{HCl \rightleftharpoons H^+ + Cl^-} \qquad \mathbf{HNO_3 \rightleftharpoons H^+ + NO_3^-}$$

$$\mathbf{H_2SO_4 \rightleftharpoons 2\ H^+ + SO_4^{--}} \qquad \mathbf{H_2CO_3 \rightleftharpoons 2\ H^+ + CO_3^{--}}$$

$$\mathbf{H_2SO_3 \rightleftharpoons 2\ H^+ + SO_3^{--}} \qquad \mathbf{HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-}$$

Some acids are highly ionized, that is, they dissociate into ions very readily. Hydrochloric, nitric and sulphuric acids are examples of acids which are highly ionized. Certain acids, on the other hand, are weakly ionized, that is, they do not dissociate into ions readily. Acetic acid, $HC_2H_3O_2$, is a good example of a weakly ionized acid.

2. Application to Bases

Previous to a consideration of the ionic theory, a base was considered as a substance which, in solution, turned red litmus blue. Now we can define a base as *a compound which gives hydroxyl ions in solution and no other negatively charged ions.* The equations for the ionization of a few bases are given below:

$$\mathbf{NaOH \rightleftharpoons Na^+ + OH^-} \qquad \mathbf{KOH \rightleftharpoons K^+ + OH^-}$$

$$\mathbf{Ca(OH)_2 \rightleftharpoons Ca^{++} + 2\ OH^-} \qquad \mathbf{NH_4OH \rightleftharpoons NH_4^+ + OH^-}$$

Some bases, such as sodium hydroxide and potassium hydroxide, are highly ionized. This means that they are readily dissociated into ions. Certain bases, such as ammonium hydroxide, are weakly ionized, that is, they do not dissociate into ions readily.

3. Application to Normal Salts

From the standpoint of the ionic theory, *a normal salt is a compound which, in solution, gives positive and negative ions other than hydrogen and hydroxyl ions.* It has been found that nearly all salts are highly ionized in water. The equations for the ionization of a few normal salts are given below:

$$NaCl \rightleftharpoons Na^+ + Cl^- \qquad Na_2SO_4 \rightleftharpoons 2\ Na^+ + SO_4^{--}$$
$$MgSO_4 \rightleftharpoons Mg^{++} + SO_4^{--} \qquad CaCl_2 \rightleftharpoons Ca^{++} + 2\ Cl^-$$

4. Application to Neutralization

In the chapter on acids, bases, and salts, it was found that the term neutralization is applied to the process in which a base is added to an acid to produce a salt and water. For example, sodium hydroxide neutralizes hydrochloric acid to form sodium chloride and water. The molecular equation for this reaction is:

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

According to the ionic theory the reaction of an acid and a base takes place between the ions and not between the molecules. It can be expressed as follows:

$$\begin{tikzcd}
HCl \arrow[r, phantom, "\rightleftharpoons"] & H^+ \arrow[r, phantom, "+"] & Cl^- \\
NaOH \arrow[r, phantom, "\rightleftharpoons"] & OH^- \arrow[r, phantom, "+"] \arrow[d, shift right] & Na^+ \arrow[d, shift right] \\
& H_2O \arrow[u, shift right] & NaCl \arrow[u, shift right]
\end{tikzcd}$$

From the above equations it is observed that the hydrogen ion of the acid combines with the hydroxyl ion of the base to form a water molecule, which is almost completely *unionized*. The sodium ion combines with the chloride ion to produce a sodium chloride molecule, which is almost completely ionized. The final solution contains chiefly three types of particles: water molecules, sodium ions, and chloride ions. Thus, the chloride ions, present in the hydrochloric acid solution, and the sodium ions, present in the sodium hydroxide solution, are unchanged during the reaction. *Neutralization is*, therefore, *the combination of the hydrogen ions of an acid with the hydroxyl ions of a base to form almost completely unionized water molecules.*

5. Application to Electrolysis of Water

It will be remembered that hydrogen and oxygen can be produced by the electrolysis of water containing a small amount of sulphuric acid, which serves as the electrolyte. The acid ionizes almost completely in water.

$$H_2SO_4 \rightleftharpoons 2\ H^+ + SO_4^{--}$$

The water, on the other hand, ionizes very slightly.

$$H_2O \rightleftharpoons H^+ + OH^-$$

The hydrogen ions are attracted to the cathode (negative) where they are discharged to form hydrogen atoms according to the following equation.

$$4\ (H^+ + \text{1 electron}) \longrightarrow 4\ H^\circ$$

The hydrogen atoms (H°) combine in pairs by the sharing of electrons to form hydrogen molecules (H_2) as follows:

$$2\ (2\ H^\circ + \text{sharing of 1 pair of electrons}) \longrightarrow 2\ H_2$$

The sulphate and hydroxyl ions, being negative, are attracted to the positive electrode (anode). It takes less electrical energy to discharge the hydroxyl ions than the sulphate ions, and so the hydroxyl ions are discharged at the anode instead of the sulphate ions. The equation for the reaction at the anode is as follows:

$$4\ (OH^- - \text{1 electron}) \longrightarrow 2\ H_2O + O_2\uparrow$$

The sulphate ions remain in the solution and they, with the help of their ionic partners (the hydrogen ions), continue to conduct the electric current from one electrode to the other. From the above discussion it is evident that the concentration of sulphuric acid in the solution would remain the same. The amount of water, however, would decrease slightly as electrolysis continued due to the conversion of part of the hydroxyl ions into oxygen, which escapes from the solution at the positive electrode.

6. Application to Electroplating

The theory of ionization can be used to explain electroplating, which is used a great deal in industry to protect metals. Let us consider silver plating which is a typical electroplating process. A bar of pure silver, which serves as the anode, is placed in a solution of some silver salt, such as silver nitrate. The object to be silver plated is also placed in the solution and it acts as the cathode. The silver nitrate solution ionizes as follows:

$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$

Direct electric current is used in this process and it must be carefully regulated to secure a satisfactory silver coating on the object, such as a silver spoon. When the current is turned on, the silver ions are attracted to the object (the cathode), and here they are discharged to form silver atoms which adhere to the spoon. In time the object becomes coated with a thin layer of metallic silver which protects it from corrosion.

At the anode, atoms of silver from the silver bar are converted into silver ions according to the following equation:

$$\underset{\text{(silver atom)}}{Ag^{\circ}} - 1 \text{ electron} \longrightarrow \underset{\text{(silver ion)}}{Ag^{+}}$$

In fact, every time a silver ion leaves the solution at the cathode, another silver ion is produced from the silver bar. Thus, the concentration of silver ions in the solution remains constant. Of course, in time the bar of silver will disappear completely and the reaction come to a stop unless the silver is replaced by another piece. This process is represented by a diagram as shown in Fig. 140. In industry the complex cyanide, $KAg(CN)_2$, is used instead of silver nitrate. Electroplating of objects with nickel or chromium is done in somewhat the same way and this process finds many useful applications in industry.

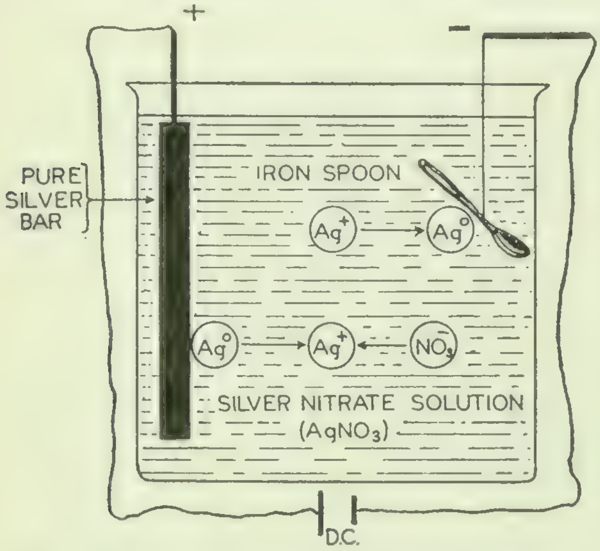


Fig. 140—Explanation of Silver Plating by Means of the Ionic Theory

7. Application to Electrolytic Refining of Copper

Copper is used a great deal in commerce as a conductor of the electric current and for this purpose the metal must be almost free of any impurities. The presence of other metals in a copper wire reduces to a marked extent its power to conduct the electric current. Copper of a high degree of purity is obtained in commerce by means of electrolytic refining.

Impure copper, known as blister copper, is shipped from the smelter to the copper refinery in large pieces, 36 inches square on the face (36″ by 36″), 1½ inches in thickness. They weigh about 700 pounds and serve as the anode in the electrolytic refining process. The inside dimensions of a commercial electrolytic cell are approximately 16½ feet long, 3½ feet wide, and 4 feet in depth. It is built of reinforced concrete and lined with an alloy of lead and antimony. The electrolyte in the cell consists chiefly of a copper sulphate solution. The current density is 17 amperes per square foot of depositing area. The cathode is a thin sheet of pure copper, 37½ inches square and 1/32 of an inch in thickness. It is known as a starter sheet and has an average weight of 11 pounds. At the beginning of the operation, each cell contains 42 anodes, 4½ inches apart, and 43 starting sheets. It takes about 33 days to completely dissolve the anode and two cathodes are made from each anode. Copper produced in this way is known as electrolytic copper and it is 99.97% pure.

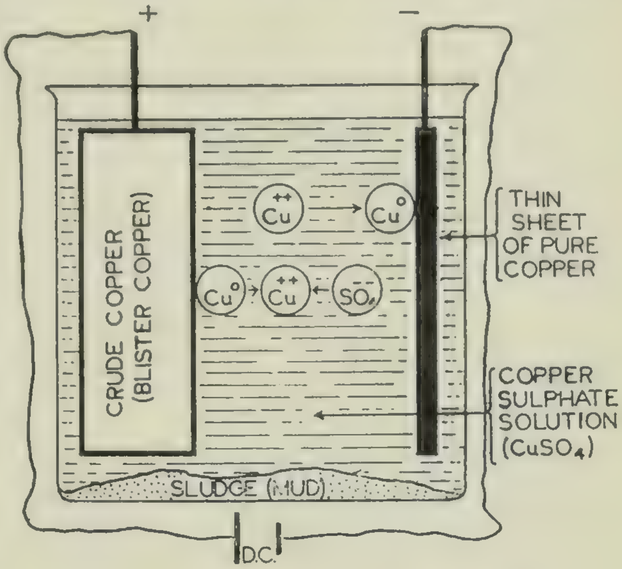

+
−
CRUDE COPPER (BLISTER COPPER)
Cu^{++}
Cu°
Cu°
Cu^{++}
SO_4
THIN SHEET OF PURE COPPER
COPPER SULPHATE SOLUTION ($CuSO_4$)
SLUDGE (MUD)
D.C.

Fig. 141—Explanation of the Electrolytic Refining of Copper by Means of the Ionic Theory

According to the ionic theory the copper sulphate ionizes in water solution as follows:

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$

The copper ion, Cu^{++}, is attracted to the cathode (negative) where it is discharged to form free copper. This can be expressed as follows:

$$\underset{\text{(copper ion)}}{Cu^{++}} + 2 \text{ electrons} \longrightarrow \underset{\text{(copper atom)}}{Cu^\circ}$$

The copper atoms adhere to the cathode and so it gradually increases in size. At the anode, copper atoms from the large piece of blister copper are changed into copper ions through the loss of electrons. This can be expressed as follows:

$$\underset{\text{(copper atom)}}{Cu^\circ} - 2 \text{ electrons} \longrightarrow \underset{\text{(copper ion)}}{Cu^{++}}$$

Every time a copper ion is discharged at the cathode, one goes into solution from the anode and so the concentration of copper ions in the solution remains the same. This process is represented by a diagram as shown in Fig. 141.

Analysis of blister copper shows that it contains traces of silver, gold, platinum, palladium, arsenic, antimony, selenium, tellurium, and several other elements. If the proper voltage is used, the metals below copper in the electromotive series do not dissolve from the anode but settle to the bottom of the cell as a sludge (mud). The metals above copper in the electromotive series dissolve but do not deposit on the cathode. The sludge, containing gold, silver, and platinum, is removed from the tanks when the anodes are used up. It is carefully refined to secure these precious metals and, in some cases, the sale of these substances pays for the entire process.

8. Hydrolysis

Some salts when dissolved in water turn red litmus blue and others turn blue litmus red. This is because certain salts react with water to form acids and bases and this type of reaction is known as *hydrolysis.* Thus, hydrolysis is the reverse of neutralization, which is the addition of an acid to a base to form a salt and water.

Sodium carbonate, washing soda, shows a basic reaction when dissolved in water. Ionic equations, to explain the reason for this, are given below.

$$\begin{array}{ccccc}
Na_2CO_3 & \rightleftharpoons & 2\,Na^+ & + & CO_3^{--} \\
2\,HOH & \longrightarrow & 2\,OH^- & + & 2\,H^+ \\
 & & \downarrow\uparrow & & \downarrow\uparrow \\
 & & 2\,NaOH & & H_2CO_3 \\
 & & \text{(strong base)} & & \text{(weak acid)}
\end{array}$$

A study of the above equations shows that sodium hydroxide, NaOH, a strong base, and carbonic acid, H_2CO_3, a weak acid, are formed when the ions of sodium carbonate and water react. Since NaOH is a strong base and H_2CO_3 is a weak acid, there would be more hydroxyl ions (OH^-) in the solution than hydrogen ions (H^+). Thus, such a solution would turn red litmus to blue.

Copper sulphate, $CuSO_4$, on the other hand, shows an acid reaction when dissolved in water. Ionic equations to explain the reason for this are given below.

$$\begin{array}{ccccc}
CuSO_4 & \rightleftharpoons & Cu^{++} & + & SO_4^{--} \\
2\,HOH & \rightleftharpoons & 2\,OH^- & + & 2\,H^+ \\
 & & \downarrow\uparrow & & \downarrow\uparrow \\
 & & Cu(OH)_2 & & H_2SO_4 \\
 & & \text{(weak base)} & & \text{(strong acid)}
\end{array}$$

A study of the above equations shows that copper hydroxide, $Cu(OH)_2$, a weak base, and sulphuric acid, H_2SO_4, a strong acid, are formed when the ions of copper sulphate and water react. Since H_2SO_4 is a strong acid and $Cu(OH)_2$ is a weak base, there would be more hydrogen ions (H^+) in the solution than hydroxyl ions (OH^-). Thus, such a solution would turn blue litmus to red.

As a rule, hydrolysis only takes place to a slight extent. For example, the hydrolysis of sodium carbonate is about 1.5 per cent. That means that only 1.5 grams of sodium carbonate out of every 100 grams are decomposed by water into sodium hydroxide and carbonic acid.

9. The Electromotive Series

Experience has shown that there are differences in the tendencies of the atoms of different metals to give up valence electrons (those in the outermost orbit) to become positive ions. Metals which react with hydrogen ions of dilute acids have a greater tendency than has hydrogen to give up electrons and so exist as ions. For example, when dilute acid is poured on zinc, since zinc has a greater tendency to give up valence electrons than has hydrogen, two hydrogen ions get two electrons from each zinc atom. In this reaction hydrogen gas is produced, and metallic zinc atoms go into solution as zinc ions.

$$Zn^\circ + 2H^+ \longrightarrow Zn^{++} + H_2\uparrow$$

A metal like copper, however, has less tendency than hydrogen to give up valence electrons. If dilute acid is added to some copper, no reaction occurs. Copper atoms do not give up their valence electrons to hydrogen and so the hydrogen ions remain in the solution. As a result of many experiments the metals have been arranged in a vertical table known as the electromotive series (see Page 76). The atoms at the top of this table have the greatest tendency to give up their valence electrons and those at the bottom the least tendency to part with valence electrons.

Any metal in the series will displace any other metal below it from the salts of the other metal. Thus, a strip of zinc metal will become coated with metallic copper when placed in a solution of a copper salt.

$$Zn^\circ + Cu^{++} \longrightarrow Zn^{++} + Cu^\circ\downarrow$$

However, if a strip of copper is placed in a solution of silver nitrate, the solution gradually becomes blue in colour indicating the presence of copper ions. The piece of copper gradually becomes smaller and metallic silver is precipitated.

$$Cu^\circ + 2\ Ag^+ \longrightarrow Cu^{++} + 2\ Ag^\circ\downarrow$$

EXERCISES

1. Define and illustrate with two examples of each the following in terms of ions: acid, base, normal salt, neutralization.
2. Use the Ionic Theory to explain the electrolysis of water, using sulphuric acid as the electrolyte. Give ionic equations in your answer.
3. Use the Ionic Theory to explain silver plating. Make a labelled diagram to illustrate your answer and give ionic equations.
4. Write a note on the electrolytic refining of copper. Illustrate your answer with a labelled diagram and ionic equations.
5. What is the difference between an atom and an ion? Illustrate by means of diagrams.

Chapter XXXVII

CHEMICAL EQUILIBRIUM

1. Factors Governing the Speed of a Chemical Reaction

The idea of equilibrium has already been encountered during the study of solutions. It was found that a saturated solution is one in which the dissolved molecules in the solution are in equilibrium with the undissolved solid molecules of the solute at a given temperature. This is an example of physical equilibrium because dissolving is a physical change. In this chapter we shall consider the important idea of chemical equilibrium. As the name suggests, this type of equilibrium deals with chemical reactions.

The question arises as to what is a chemical reaction. The answer is that it is a chemical change in which new molecules are produced. The tendency for substances to react is measured by the *speed* of a reaction. *The term speed means the amount of materials changed into new substances in a unit of time*, such as the second, minute, hour, or day. It is important to remember that the speed of a reaction depends upon the number of collisions taking place between molecules or ions in a unit of time. The number of collisions can be increased in various ways and some of the chief factors governing the speed of a reaction are:

(1) Temperature. In general, it has been found that chemical reactions go more rapidly at high temperatures than at low temperatures. The speed of a reaction is doubled approximately for an increase of 10°C.

(2) Catalysts. Certain substances, known as catalysts, alter the speed of reactions. As a rule, a catalyst increases the speed but some, however, retard the speed of a reaction.

(3) Molecular Concentration. Let us suppose that substance A reacts with substance B to produce two new substances, C and D. If we increase the molecular concentration of A, then there will be more chances of A molecules colliding with B molecules, and so more molecules of C and D will be formed. In other words, the speed of the reaction is increased by the addition of more of A. It could also be increased by the addition of more B molecules. In 1863, Guldberg and Waage,

discovered a law concerning this. It is known as the *Law of Molecular Concentrations* or the *Law of Mass Action.* The law states that *the speed of a chemical reaction is proportional to the product of the molecular concentrations of the reacting substances.* In mathematical terms it can be expressed as follows:

$$S \underset{\text{(varies as)}}{\propto} [A] \times [B]$$

Where S = speed of the reaction.
[A] = molecular concentration of A
[B] = molecular concentration of B

Chemical reactions can be divided into two chief kinds, reversible and irreversible. Reversible reactions are those in which the products tend to react with themselves to form the starting materials. They can also be considered as reactions which will go in either direction depending on the conditions, such as temperature, concentration, etc. Irreversible reactions, on the other hand, are those which do not reverse to any appreciable extent, and they are said to go to completion. In theory all reactions are reversible but some are so slightly reversible that we call them irreversible.

2. Reversible Reactions

Many examples of reversible reactions have already been encountered and equations for a few are given below:

$$2\ HgO \rightleftharpoons 2\ Hg + O_2$$

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

$$N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3$$

$$HCl \rightleftharpoons H^+ + Cl^-$$

$$3\ Fe + 4\ H_2O \rightleftharpoons Fe_3O_4 + 4\ H_2$$

All reversible reactions are indicated in equations by means of double arrows.

3. Chemical Equilibrium

Let us consider the case of the reaction between two substances A and B to form two new substances C and D. Let us assume that C and D react to give back the starting materials. These two reactions can be expressed separately as follows:

(1) $A + B \longrightarrow C + D$
(2) $C + D \longrightarrow A + B$

or they can be expressed in one equation:

$$A + B \rightleftharpoons C + D$$

It is important to realize that in a reversible reaction there are two opposing tendencies. Here we have the tendency of A and B to react to produce the new substances C and D. We also have the opposing tendency of C and D to react to form the starting materials A and B.

Let S_1 = the speed of the forward reaction.
Let S_2 = The speed of the backward reaction.

In time S_1 will equal S_2, and when such a *condition* or *state of affairs* is reached, we have a chemical equilibrium.

4. Factors Shifting the Point of Equilibrium

(1) CONCENTRATION.

$$\underset{\text{(ferric chloride)}}{FeCl_3} + \underset{\text{(potassium sulphocyanate)}}{3\ KSCN} \rightleftharpoons \underset{\substack{\text{(ferric sulphocyanate)} \\ \text{(red)}}}{Fe(SCN)_3} + \underset{\text{(potassium chloride)}}{3\ KCl}$$

The above equation represents a reaction in chemical equilibrium. Addition of more ferric chloride, $FeCl_3$, shifts the point of equilibrium to the right as indicated by a deepening of the red colour which is due to the ferric sulphocyanate, $Fe(SCN)_3$. Addition of more potassium sulphocyanate, KSCN, to the equilibrium mixture also shifts the reaction to the right. On the other hand, the addition of a saturated solution of potassium chloride, KCl, to the equilibrium mixture shifts the reaction to the left as shown by a decrease in the red colour.

(2) PRESSURE. This factor applies only to gases. Pressure displaces the equilibrium in the direction of those gases having the smaller volume.

$$3\ H_2 + N_2 \rightleftharpoons 2\ NH_3$$

For example, in the reaction represented by the above equation, an increase of pressure causes an increase in the yield of ammonia, NH_3.

(3) TEMPERATURE. It has been found that the addition of heat to an equilibrium mixture speeds up that reaction which takes place with the absorption of heat. Let us consider an equilibrium consisting of four substances, A, B, C, and D.

$$A + B \rightleftharpoons C + D$$

Let us suppose that A reacts with B to give C + D with the evolution of heat; that is, it is an exothermic reaction.

$$A + B \longrightarrow C + D + \text{heat}$$

C and D, on the other hand, react to give A + B with the absorption of heat. It is an endothermic reaction.

$$C + D + \text{heat} \longrightarrow A + B$$

Thus, in this equilibrium the addition of heat would cause the equilibrium to shift to the left.

(4) CATALYST. A catalyst does not shift the equilibrium point. It simply causes the reaction to reach equilibrium in a shorter time. It is interesting to know that at equilibrium, a catalyst favours the backward and forward reactions to the same extent.

5. Conditions Necessary to cause Reactions to go to Completion

Reactions which go in both directions and which come to equilibrium are not suitable for use in industrial chemistry. Therefore, the aim in industrial processes is to select irreversible reactions, or to deal with reversible ones so as to make them go in the desired direction. The conditions required to cause reactions to go to completion are:

(1) IF ONE PRODUCT IS A GAS. If a gas is produced as a result of a reaction, it is likely to leave the reaction mixture. Of course, if it leaves the field of action, the backward reaction is impossible. The following equations represent reactions of this type.

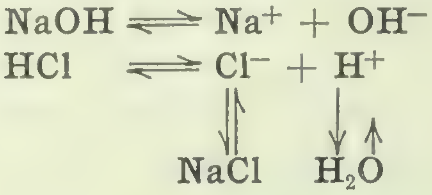
$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2\uparrow$$
$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + CO_2\uparrow$$
$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl\uparrow$$
$$MnO_2 + 4\,HCl \longrightarrow MnCl_2 + 2\,H_2O + Cl_2\uparrow$$

(2) IF ONE PRODUCT IS A PRECIPITATE. If one of the products of a reaction happens to be a precipitate (insoluble), the reaction goes to completion since the precipitate settles to the bottom of the reaction mixture. Thus, it leaves the scene of activity, and so the reaction is irreversible. The following equations represent reactions of this kind.

$$AgNO_3 + NaCl \longrightarrow AgCl\downarrow + NaNO_3$$
$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2\,HCl$$

(3) IF ONE PRODUCT IS ONLY SLIGHTLY IONIZED. During the study of the ionic theory it was found that reactions of electrolytes are between the ions, and not between the molecules. If, in such a reaction, two ions combine to form a slightly ionized molecule, these ions are locked up in the molecule, and so they are unable to take any further part in the

reaction. This would tend to make the reaction go to completion. The neutralization of acids by bases is a good example of this type of reaction. The ionic equations for the neutralization of sodium hydroxide by hydrochloric acid are given below:



$$\begin{tikzcd}[column sep=small]
NaOH \arrow[r, harpoon, shift left] & Na^+ \arrow[l, harpoon, shift left] & + & OH^- \\
HCl \arrow[r, harpoon, shift left] & Cl^- \arrow[l, harpoon, shift left] \arrow[d, shift right] & + & H^+ \arrow[d, shift right] \\
& NaCl \arrow[u, shift right] & & H_2O \arrow[u, shift right]
\end{tikzcd}$$

The hydroxyl ions of the base combine with the hydrogen ions of the acid to form molecules of water which are only very slightly ionized. In this way the hydrogen and hydroxyl ions are almost completely removed from the scene of activity. They are locked up in the water molecules and so the reaction goes to completion.

EXERCISES

1. Explain what is meant by physical equilibrium. Illustrate your answer with one example.
2. (a) What is meant by the speed of a reaction?
   (b) Discuss briefly the speed of a reaction from the standpoint of the molecular theory.
3. (a) What factors govern the speed of a reaction?
   (b) What is the Law of Mass Action?
4. (a) What are reversible reactions?
   (b) Write equations for five reversible reactions.
5. (a) Explain carefully what is meant by chemical equilibrium.
   (b) What factors shift the point of equilibrium?
6. Under what conditions will reactions go to completion? Give two equations for each condition.

Chapter XXXVIII

AMMONIA

1. Occurrence

Small amounts of ammonia are present in the atmosphere and in natural waters. It is formed in nature when certain bacteria bring about the decay of proteins, which are complex organic compounds found in plants and animals. The ammonia so produced is often changed by another type of bacteria into compounds which are beneficial to the growth of plants. The plants, in turn, manufacture proteins, which upon decay produce ammonia again. This is part of the nitrogen cycle which is so important in nature. A diagram of the nitrogen cycle is shown in Fig. 142.

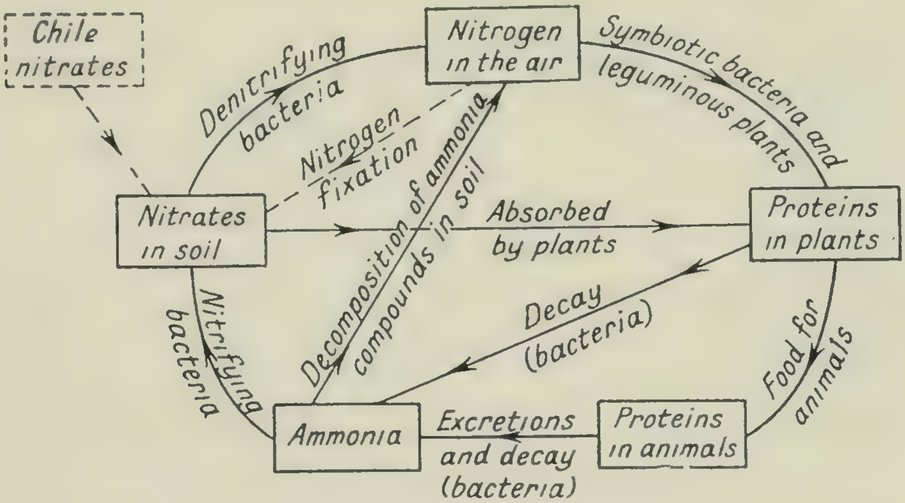


Fig. 142—The Nitrogen Cycle

2. Preparation

(1) Laboratory Method of Preparation. The usual laboratory method of preparing ammonia consists of heating a solution of an ammonium compound with a strong base. For example, the heating of a mixture of quicklime (calcium oxide), ammonium chloride, and water, produces ammonia gas readily. The equations for the reactions involved are:

$$CaO + HOH \longrightarrow Ca(OH)_2$$

$$Ca(OH)_2 + 2\ NH_4Cl \longrightarrow 2\ NH_4OH + CaCl_2$$

$$2\ NH_4OH \longrightarrow 2\ NH_3\uparrow + 2\ H_2O$$

An apparatus which can be used for this preparation is shown in Fig. 143.

It is important to know that the heating of *any ammonium compound with a strong base* produces ammonia gas. Equations for several reactions, which result in the production of ammonia, are given below.

$$NH_4Cl + NaOH \longrightarrow NH_4OH + NaCl$$
$$NH_4OH \longrightarrow NH_3\uparrow + H_2O$$
$$(NH_4)_2SO_4 + 2\,KOH \longrightarrow 2\,NH_4OH + K_2SO_4$$
$$2\,NH_4OH \longrightarrow 2\,NH_3\uparrow + 2\,H_2O$$
$$NH_4NO_3 + NaOH \longrightarrow NH_4OH + NaNO_3$$
$$NH_4OH \longrightarrow NH_3\uparrow + H_2O$$

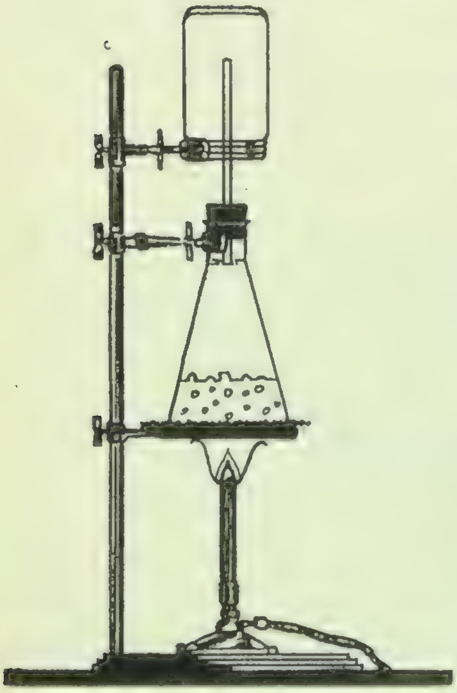


Fig. 143
The Laboratory Preparation and Collection of Ammonia Gas by the Downward Displacement of Air

(2) Industrial Methods of Preparation. (a) *As a by-product in manufacture of coal-gas.* When coal is subjected to the process of destructive distillation (heating in absence of air), it gives off a mixture of gases. Cooling of this mixture brings about the condensation of a black liquid, known as coal-tar, from which chemists can extract many useful and important compounds. The gases which are not condensed by the cooling process consist chiefly of ammonia gas and coal-gas. These two gases can be separated by passing them through water. The ammonia dissolves but the coal-gas, being insoluble in water, does not. The coal-gas burns readily and so can be used as a fuel. The ammonia solution is often treated with sulphuric acid to produce ammonium sulphate, $(NH_4)_2SO_4$, which is an important component of commercial fertilizers.

$$2\,NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

(b) *The Haber Process (The Synthetic Ammonia Process).*

$$\underset{\text{(3 volumes)}}{3\,H_2} + \underset{\text{(1 volume)}}{N_2} \rightleftharpoons \underset{\text{(2 volumes)}}{2\,NH_3} + 24{,}000 \text{ calories}$$

The above reaction was studied carefully by the German chemist, Haber, and, in 1913, he discovered the necessary conditions to make it an industrial process. It was found in the chapter on chemical equilibrium that when pressure is applied to a reaction in equilibrium such as the above, the reaction goes in the direction which produces the smaller volume. In this case, pressure on the system in equilibrium would cause the reaction to go to the right. Pressures varying from 1,500 to 15,000 lb. per square inch are used today. The reaction is carried out in a container, known as a converter, which is made of special chrome-vanadium alloy steel. This material can withstand the action of hot hydrogen under high pressures. Since heat is liberated, the above reaction is not favoured by too high a temperature. The temperature found most suitable is about 500° C. It will be recalled that a catalyst does not shift the equilibrium point of a reaction, but it does cause the reaction to come to equilibrium quickly. One of the best catalysts for this process consists of porous iron containing small quantities of potassium and aluminum oxides. The amounts of ammonia obtained depend upon the pressure used, as well as the time of contact of the mixture of hydrogen and nitrogen with the catalyst. As a rule, from about 5 per cent to 25 per cent of the gases which enter the converter are changed into ammonia gas.

It is quite easy at high pressures and at low temperatures to change ammonia gas to a liquid, and this is a very common method of removing the ammonia from the mixture which leaves the converter. Another method consists of passing the escaping gases through water. The ammonia dissolves very readily in water but nitrogen and hydrogen are almost completely insoluble in water. Of course, the unchanged hydrogen and nitrogen are returned to the converter to be passed over the catalyst again. A diagram of this process is shown in Fig. 144.

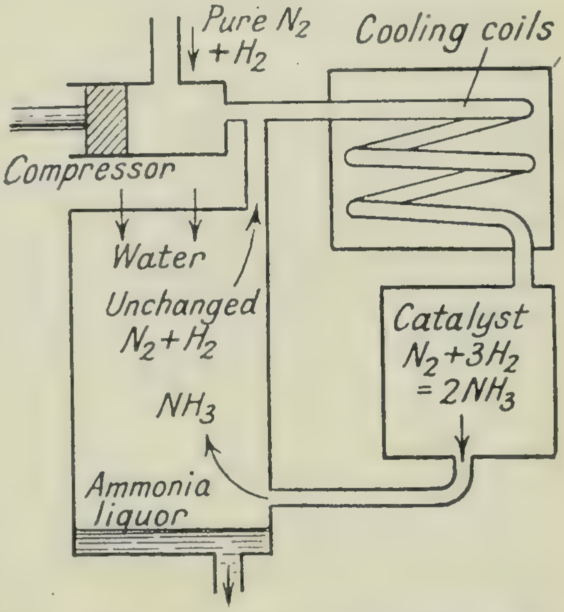


Fig. 144—The Haber Process of Making Ammonia, (One Method of Nitrogen Fixation)

Before World War I, the chief industrial method of producing nitric acid consisted of heating Chile saltpetre, sodium nitrate ($NaNO_3$), with concentrated sulphuric acid. Nitric acid is needed in the manufacture of nearly all high explosives, and so Chile saltpetre was a very important chemical in time of war. When the war started the Germans attempted, without success, to keep all British and French shipping from transporting Chile saltpetre to Europe. In a short time after hostilities had commenced, the allied blockade prevented Germany from securing the nitrate. It was hoped by the allied leaders that this would shorten the conflict by several years. Unfortunately for the allied cause, Haber was able to produce ammonia by his method from the nitrogen of the air and hydrogen, obtained by an inexpensive method. Ostwald, another German chemist, had previously devised a method for oxidizing ammonia to nitric acid, and so the Germans had an unlimited supply of nitric acid at their disposal. This meant that they had plenty of high explosives to carry on the war.

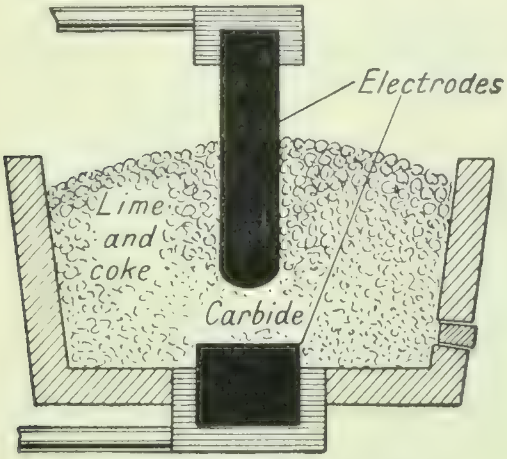


Fig. 145—Manufacture of Calcium Carbide

The synthesis of ammonia from its elements is the chief process for the fixation of nitrogen. *Fixation is the changing of the nitrogen of the air into compounds which can be used in industry and in agriculture.*

(c) *The Cyanamide Process.* The first stage in this process consists in the manufacture of calcium carbide. This substance is made by heating a mixture of lime and coke in an electric furnace as shown in Fig. 145.

$$\mathbf{CaO + 3\ C + 121{,}000\ cal. \longrightarrow \underset{\text{(calcium carbide)}}{CaC_2} + CO\uparrow}$$

The equation shows that the reaction is decidedly endothermic, and so needs great amounts of energy.

The next step in the process consists of heating the carbide with nitrogen.

$$\mathbf{CaC_2 + N_2 \longrightarrow \underset{\text{(calcium cyanamide)}}{CaCN_2} + C + heat}$$

The above reaction is an exothermic one and this means that once it is started, no further heat is required. The nitrogen used in this stage of the process must be separated from the oxygen of the air. This is done by fractional distillation of liquid air.

The third step consists of treating calcium cyanamide with steam under pressure to produce ammonia gas.

$$CaCN_2 + 3\ H_2O \longrightarrow CaCO_3 + 2\ NH_3\uparrow$$

The above reaction takes place slowly when cyanamide is exposed to the water of the soil and of the air, and so this substance may, therefore, be used without any further treatment as a fertilizer.

3. Physical Properties

(1) Ammonia is a gas under ordinary conditions of temperature and pressure.
(2) It is colourless.
(3) The gas has a very penetrating odour (once experienced you do not forget it).
(4) Ammonia is lighter than air, one litre weighing about 0.77 grams.
(5) It is very soluble in water, one litre of water dissolving about 1300 litres of the gas at 0° C. This property can be demonstrated experimentally by the apparatus shown in Fig. 146, which can also be used to show that hydrogen chloride gas is extremely soluble.

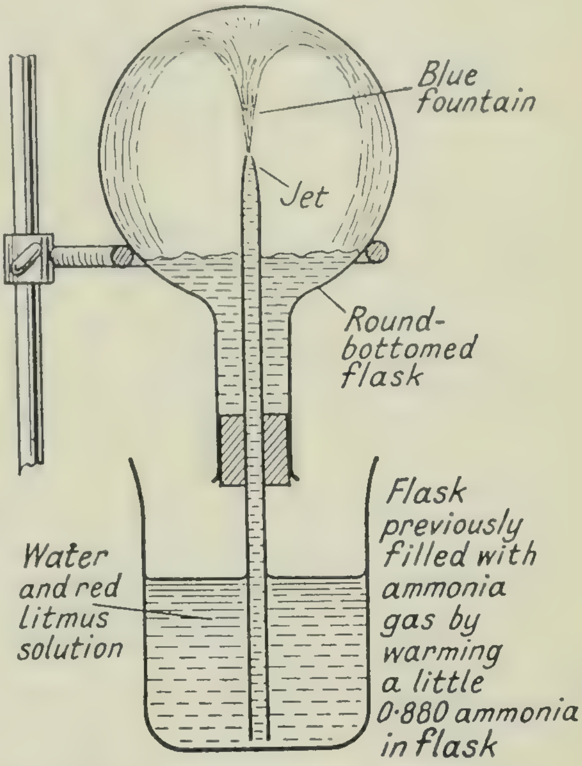

Blue fountain
Jet
Round-bottomed flask
Flask previously filled with ammonia gas by warming a little 0·880 ammonia in flask
Water and red litmus solution

Fig. 146—The Solubility of Ammonia

(6) Ammonia can be changed to a liquid quite readily. For example, at 20°C. it requires only about 8.5 atmospheres of pressure to convert the gas to a colourless liquid, which boils under a pressure of one atmosphere at −33°C.

4. Chemical Properties

(1) Ammonia does not support combustion.
(2) It does not burn in air, but does in pure oxygen with a yellow flame. Water vapour and nitrogen are the chief products of the reaction.

$$4\ NH_3 + 3\ O_2 \longrightarrow 6\ H_2O + 2\ N_2\uparrow$$

Platinum gauze serves as a catalyst to oxidize ammonia to nitric oxide (NO). This process is one of the chief industrial methods of producing nitric acid (HNO_3) and it will be described later. The equation for the reaction is as follows:

$$4\ NH_3 + 5\ O_2 \longrightarrow 6\ H_2O + \underset{\text{(nitric oxide)}}{4\ NO}$$

(3) When ammonia is passed over certain metallic oxides it acts as a reducing agent. For example, if dry ammonia gas is passed over heated copper oxide, the ammonia is oxidized and the copper oxide reduced:

$$3\ CuO + 2\ NH_3 \longrightarrow 3\ Cu + N_2\uparrow + 3\ H_2O$$

(4) Ammonia gas combines with hydrogen chloride gas to form a white smoke, consisting of very fine solid particles of ammonium chloride (NH_4Cl).

$$NH_3 + HCl \longrightarrow NH_4Cl$$

The characteristic odour of ammonia, along with the above reaction, serves as a test for the gas.

(5) Ammonia combines with water to form a weak base, known as ammonium hydroxide (aqua ammonia).

$$NH_3 + H_2O \rightleftharpoons \underset{\text{(ammonium hydroxide)}}{NH_4OH}$$

Ammonium hydroxide is weakly ionized into ammonium (NH_4^+) and hydroxyl (OH^-) ions according to the following equation.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

5. Chemical Test for the Ammonium Ion

The ammonium ion can be detected by heating the compound under consideration with some strong base, such as sodium hydroxide. If the gas which escapes from this reaction has the penetrating odour of ammonia, and if it turns moist red litmus blue, then the compound contains ammonium ions. For example, ammonium chloride, when warmed with sodium hydroxide, produces ammonia gas which turns moist red litmus blue. The following equations represent the reactions involved in the above example.

$$NH_4Cl + NaOH \longrightarrow NH_4OH + NaCl$$
$$NH_4OH \rightleftharpoons NH_3 + H_2O$$

The escaping ammonia comes in contact with the water on the litmus, and so produces ammonium hydroxide, which ionizes to form ammonium and hydroxyl ions. The hydroxyl ions turn the red dye in the litmus paper to a blue dye.

6. Uses of Ammonia

(1) In Preparation of Nitric Acid. The use of ammonia in the preparation of nitric acid by the Ostwald Process is, perhaps, the most important use of this gas.

(2) IN REFRIGERATION. All liquids remove heat from their surroundings upon evaporation. Liquid ammonia does this to a marked extent, and so it is employed in large refrigeration units, such as those used in meat packing plants and in making artificial ice. The liquid ammonia is forced through coils of pipe and, as it passes along, evaporation takes place. This process removes much heat from whatever material surrounds the coils, cooling it to a low temperature. The coils containing the evaporating liquid ammonia are surrounded, as a rule, by a concentrated solution of calcium chloride, which can be cooled to quite a low temperature without freezing. Ice can be secured by freezing pure water held in containers which are placed in the cold calcium chloride solution. In refrigerating plants and skating rinks the cold chloride solution is circulated in pipes through the places to be cooled. The ammonia gas, produced by the evaporation of the liquid in the coils, is conducted into a compressor where it is changed back to the liquid state again. It is now ready to be used again in the cooling process. A diagram of this process is shown in Fig. 147.

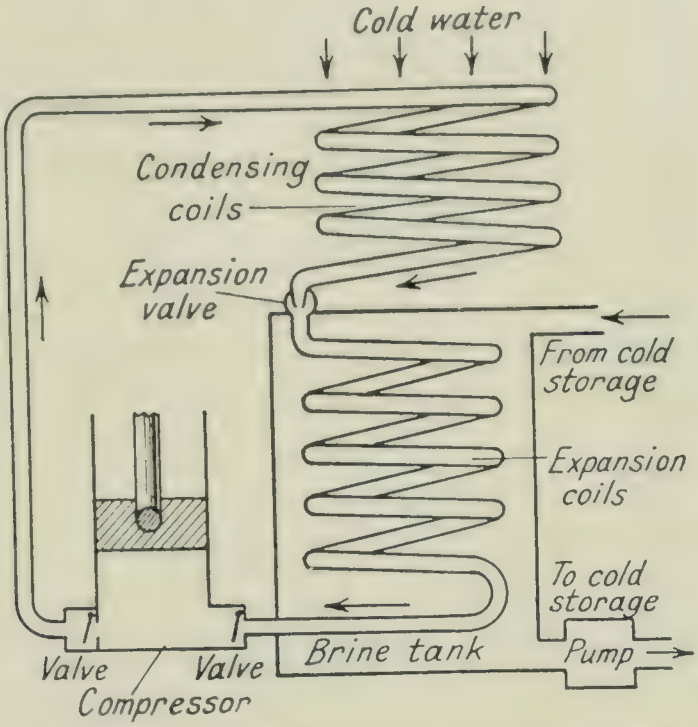


FIG. 147—A REFRIGERATOR USING AMMONIA AS THE COOLING MATERIAL

(3) IN THE MANUFACTURE OF WASHING SODA. Washing soda, sodium carbonate, Na_2CO_3, is usually prepared commercially by the Solvay Process, which consists of bubbling ammonia and carbon dioxide into a saturated solution of sodium chloride. Sodium carbonate has many important uses in industry.

(4) To Prepare Ammonium Salts. Some ammonium salts, such as ammonium sulphate, $(NH_4)_2SO_4$, are important fertilizers. Sal ammoniac (NH_4Cl) is used in the manufacture of certain kinds of dry cell batteries. Ammonium nitrate (NH_4NO_3) is used to make some explosives. The chief component of smelling salts is ammonium carbonate, $(NH_4)_2CO_3$, which decomposes even at room temperature into ammonia and ammonium bicarbonate.

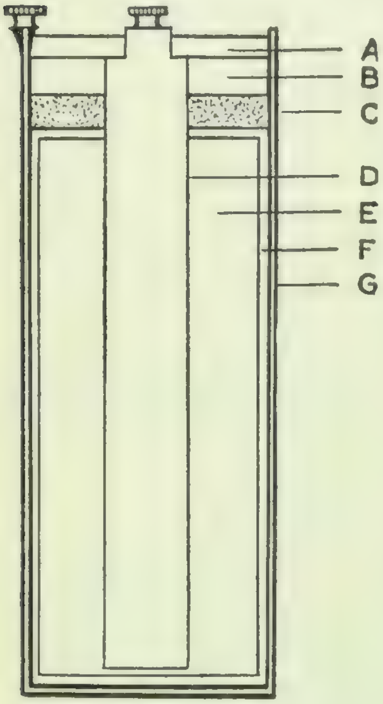


Fig. 148—Cross-Section of a Dry Cell

A, sealing wax; B, tar; C, sand; D, carbon; E, paste containing *sal ammoniac* (NH_4Cl); F, cardboard; G, zinc.

$$(NH_4)_2CO_3 \longrightarrow NH_3\uparrow + \underset{\text{(ammonium bicarbonate)}}{NH_4HCO_3}$$

(5) To Make Aqua Ammonia. A solution of ammonia in water is known commercially as aqua ammonia and it is used in cleaning and as a water softener in the home and in industry.

AMMONIUM HYDROXIDE

1. Preparation

Ammonium hydroxide is prepared by passing ammonia gas into water.

$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

It is the hydroxyl ion (OH^-) which gives ammonium hydroxide its basic properties.

2. Chief Properties

(1) Ammonium hydroxide is *unstable*, decomposing even at room temperature into ammonia and water.

$$NH_4OH \longrightarrow NH_3\uparrow + H_2O$$

This is the reason that the odour of ammonia gas is always observed when the stopper is removed from a bottle of ammonium hydroxide.

(2) *It reacts with acids*, in the same way that other bases do, to form salts. These salts are known as the ammonium salts. Equations representing the neutralization of three common acids by this base are given below.

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$

$$NH_4OH + HNO_3 \longrightarrow NH_4NO_3 + H_2O$$

$$2\ NH_4OH + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + 2\ H_2O$$

It will be observed that all of the salts produced in the above reactions contain a group of atoms known as the ammonium radical (NH_4). It is often called a metallic radical since it behaves in reactions like a metal. The ammonium radical is not known in the free state and it has a valence of one positive.

3. Uses

(1) *Cleansing agent.* It is good for this purpose, removing grease and dirt readily.

(2) *To make ammonium salts.* Several examples of this use have already been given in this chapter.

(3) *In washing.* Ammonium hydroxide, known commercially as aqua ammonia, is used in washing to a considerable extent in the home and in industry to soften hard water.

EXERCISES

1. Write a short note on the nitrogen cycle in nature.
2. (a) What is the general method of preparing ammonia in the laboratory?
   (b) Write two equations to illustrate the method given in (a).
   (c) Make a labelled drawing of the apparatus used in (a).
3. Discuss the manufacture of ammonia from coal.
4. Discuss carefully the Haber Process.
5. Write equations to illustrate the three steps of the Cyanamide Process.
6. Tabulate five physical and four chemical properties of ammonia.
7. What is the chemical test for the ammonium ion?
8. Tabulate four uses of ammonia.
9. (a) How is ammonium hydroxide prepared?
   (b) What are the chief properties of this base?
   (c) Why is the ammonium group called a metallic radical?
   (d) Give three uses of ammonium hydroxide.
10. (a) What is meant by nitrogen fixation?
    (b) Give two examples of this process.

CHAPTER XXXIX

NITRIC ACID

1. Preparation

(1) LABORATORY METHOD. Many years ago the alchemists, those pioneers of chemistry, discovered a method of preparing nitric acid (aqua fortis) by the action of sulphuric acid on saltpetre. They used an apparatus similar to the one shown in Fig. 149. The laboratory method used today consists of heating a mixture of Chile saltpetre, sodium nitrate ($NaNO_3$), and concentrated sulphuric acid, in a glass retort, as shown in Fig. 150. If the temperature is kept low, and if an excess of the acid is used, the following reaction takes place.

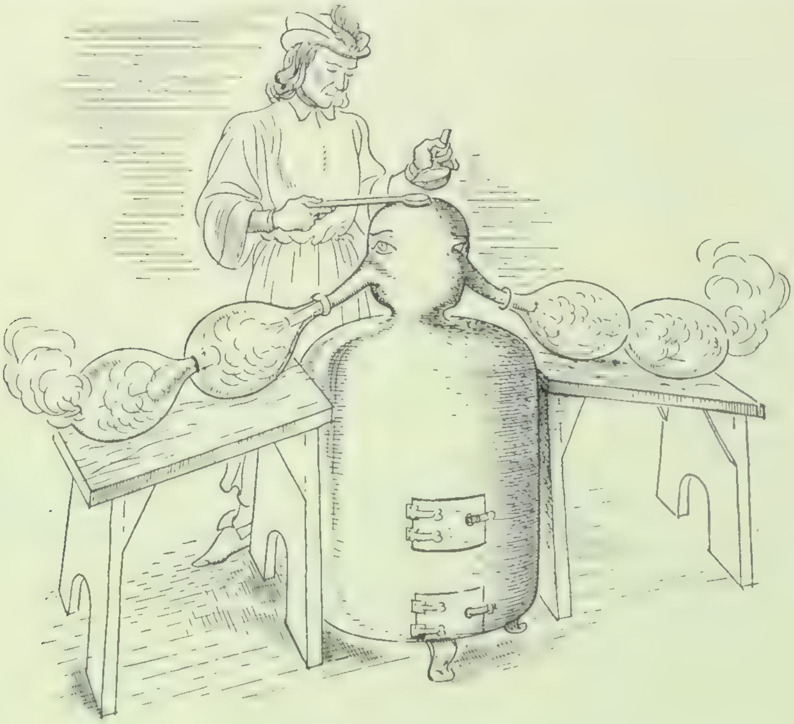


FIG. 149

Apparatus, known as the Iron Man with the two noses, used by the alchemists for the preparation of nitric acid by the action of sulphuric acid on saltpetre.

$$\mathbf{NaNO_3 + H_2SO_4 \longrightarrow \underset{\text{(sodium hydrogen sulphate)}}{NaHSO_4} + HNO_3\uparrow}$$

When there is an excess of sodium nitrate and if a higher temperature is used, a second reaction occurs between the sodium hydrogen sulphate and more sodium nitrate.

$$\mathbf{NaNO_3 + NaHSO_4 \longrightarrow Na_2SO_4 + HNO_3\uparrow}$$

As a rule, this second reaction is avoided, if possible, because the higher temperature decomposes the nitric acid to a considerable extent. Nitric acid is also prepared commercially by the above method, the retort being made of cast iron, and the condenser of some acid resistant material, such as duriron, glass, or stoneware. A diagram of such a plant is shown in Fig. 151.

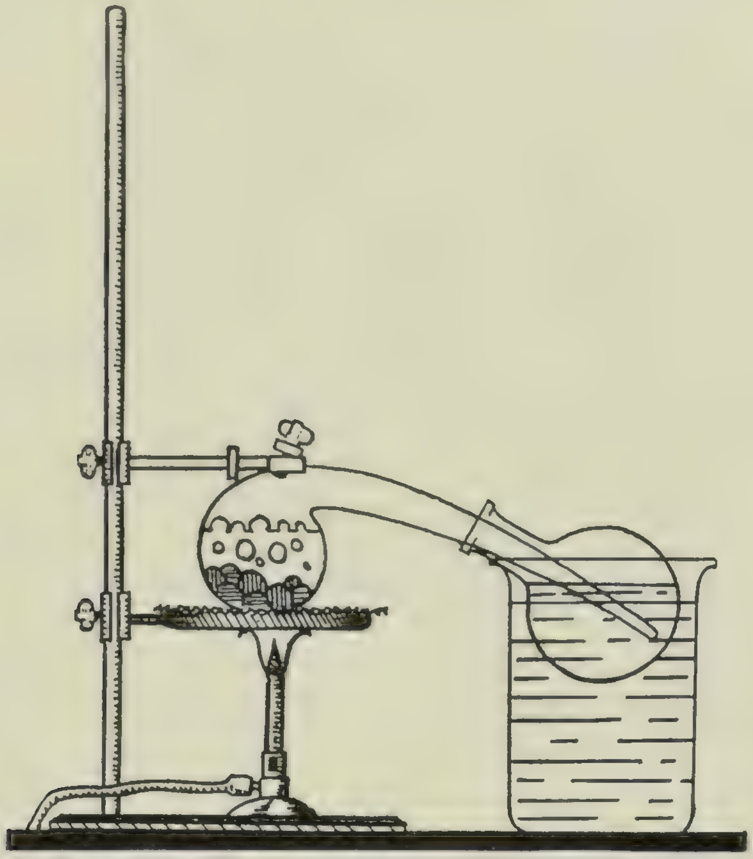


FIG. 150—LABORATORY PREPARATION OF NITRIC ACID, USING A RETORT

(2) INDUSTRIAL METHODS. (*a*) *The Ostwald Process*. It has already been mentioned in the previous chapter that a German

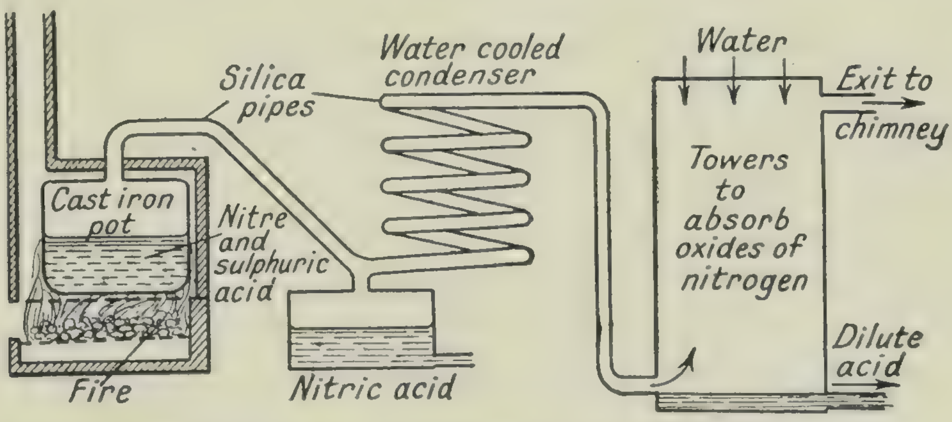


FIG. 151—THE INDUSTRIAL PREPARATION OF NITRIC ACID FROM CHILE SALTPETRE (NITRE) AND SULPHURIC ACID

chemist, Ostwald, developed a method of oxidizing ammonia to nitric acid. The catalyst used is platinum gauze, and it is customary to use air as a source of oxygen, with ten volumes of air per one volume of ammonia. The best temperature appears to be about 700° C. and the conversion is approximately 95 per cent. Equations for the reactions taking place in this process are as follows:

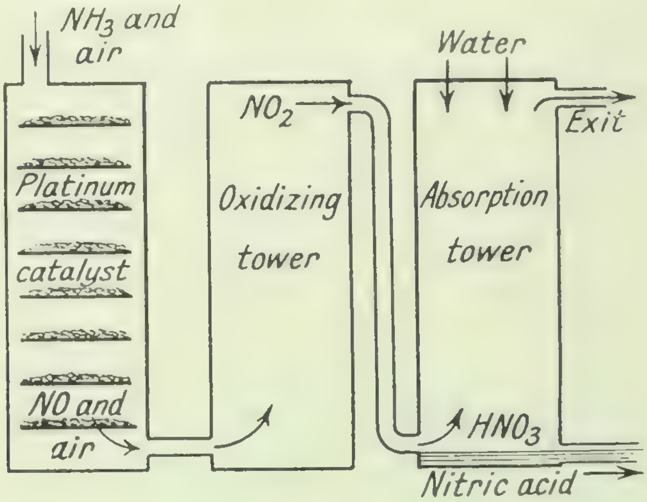


FIG. 152—THE OSTWALD PROCESS OF MAKING NITRIC ACID FROM AMMONIA

(1) $\mathbf{4\ NH_3 + 5\ O_2 \longrightarrow 6\ H_2O + \underset{\text{(nitric oxide)}}{4\ NO}}$

The nitric oxide is at once changed into nitrogen dioxide (NO_2) by combining with oxygen of the air, on cooling.

(2) $\mathbf{2\ NO + O_2 \longrightarrow \underset{\text{(nitrogen dioxide)}}{2\ NO_2}}$

The nitrogen dioxide is then passed into warm water.

(3) $\mathbf{3\ NO_2 + H_2O \longrightarrow 2\ HNO_3 + NO}$

The nitric oxide produced in reaction (3) is returned to the process and changed into NO_2. A diagram of this process is shown in Fig. 152.

(*b*) *The Birkeland and Eyde Process.* This is the earliest of the modern processes. However, it has not been able to compete with the Ostwald process, and so it is no longer used. It has been known for many years that during an electric storm a small amount of nitric acid is formed. In an attempt to imitate nature in producing nitric acid, two Norwegian chemists, Birkeland and Eyde, in 1903, devised a method of preparing nitric acid by passing powerful electric sparks through air. It has been estimated that temperatures from about 3200° C. to 3500° C. are reached in the electric arc, spread out into a circular disk by electro-magnets. The equations for the reactions involved are:

(1) $$N_2 + O_2 + \underset{\text{(electric arc)}}{\text{high temperatures}} \longrightarrow 2\,NO$$

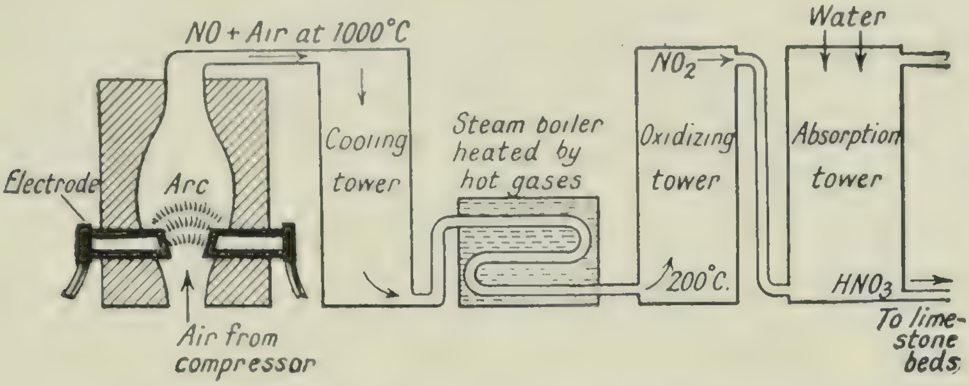


FIG. 153—THE BIRKELAND AND EYDE PROCESS OF MAKING NITRIC ACID BY PASSING AN ELECTRIC ARC THROUGH AIR

The gases escaping from the arc are cooled rapidly and the nitric oxide combines with oxygen of the air.

(2) $$2\,NO + O_2 \longrightarrow 2\,NO_2$$

The NO_2 is then added to warm water to form a weak solution of nitric acid.

(3) $$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO$$

As already mentioned this process is no longer used commercially, but it is considered here because of its importance in nature. Nitric acid produced during electric storms is carried by rain water through the soil. All soils contain limestone, calcium carbonate, and this compound reacts with the nitric acid to form calcium nitrate, water, and carbon dioxide.

$$CaCO_3 + 2\,HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O + CO_2\uparrow$$

Calcium nitrate is an important fertilizer, and so nature enriches the soil in this way.

2. Physical Properties

(1) Nitric acid is a *colourless liquid* when pure.
(2) It has a sharp, choking odour.
(3) The liquid is heavier than water, having a density of 1.52.
(4) Nitric acid is soluble in water in all proportions.
(5) It boils at 86° C.

3. Chemical Properties

(1) Stability. Nitric acid is a relatively *unstable* compound. On heating it decomposes rapidly according to the following equation.

$$4\ HNO_3 \longrightarrow 2\ H_2O + 4\ NO_2\uparrow + O_2\uparrow$$

It also decomposes slowly in the same way when exposed to sunlight. Nitrogen dioxide, NO_2, is a brown gas, which is quite soluble in nitric acid, and so when nitric acid is exposed to light for some time or heated, it has a yellowish or brownish colour.

(2) Acid Properties. In solution nitric acid is almost completely ionized,

$$HNO_3 \longrightarrow H^+ + NO_3^-$$

and so it has all the properties of a typical acid. It reacts with all the metals except platinum and gold, producing a nitrate and various other substances, the formation of which depend upon the metal used, the concentration of the acid, and the temperature of the reaction. No hydrogen is liberated in these reactions, as a rule, because nitric acid is such a strong oxidizing agent that any hydrogen formed is oxidized at once to water.

$$2\ HNO_3 + 3\ H_2 \longrightarrow 4\ H_2O + 2\ NO$$

It is only when very dilute nitric acid is added to a metal, above hydrogen in the electromotive series, that free hydrogen is liberated. Of course, nitric acid reacts with bases to form a class of salts, known as nitrates. For example, sodium nitrate, $NaNO_3$, is formed by the action of nitric acid on sodium hydroxide.

$$HNO_3 + NaOH \longrightarrow NaNO_3 + H_2O$$

Nitrates are also produced when nitric acid reacts with carbonates. Thus, the addition of nitric acid to calcium carbonate gives calcium nitrate, carbon dioxide, and water.

$$CaCO_3 + 2\ HNO_3 \longrightarrow Ca(NO_3)_2 + H_2CO_3$$

$$H_2CO_3 \longrightarrow H_2O + CO_2\uparrow$$

(3) Oxidizing Agent. Nitric acid is a powerful oxidizing agent, oxidizing metals, non-metals, and many organic substances. Nitric acid oxidizes all the metals in the electromotive series except platinum and gold. The concentration of the acid has a marked effect on the nature of the products formed when nitric acid reacts with metals. For example, with copper, if the acid is *concentrated*, the gas which escapes from the reaction

mixture is chiefly the brown gas, nitrogen dioxide (NO_2). The equation for this reaction is as follows:

$$Cu + \underset{\substack{\text{(concentrated}\\\text{nitric acid)}}}{4\ HNO_3} \longrightarrow Cu(NO_3)_2 + 2\ H_2O + \underset{\substack{\text{(nitrogen}\\\text{dioxide)}}}{2\ NO_2\uparrow}$$

On the other hand, if the nitric acid is *dilute*, the gas which is produced is chiefly the colourless gas, nitric oxide (NO). The equation for this reaction is given below:

$$3\ Cu + \underset{\substack{\text{(dilute}\\\text{nitric acid)}}}{8\ HNO_3} \longrightarrow \underset{\substack{\text{(nitric}\\\text{oxide)}}}{2\ NO} \uparrow + 3\ Cu(NO_3)_2 + 4\ H_2O$$

Concentrated nitric acid oxidizes certain non-metals, such as carbon, sulphur, and phosphorus. For example, with red hot charcoal (carbon) the acid is reduced to nitrogen dioxide, and the carbon is oxidized to carbon dioxide.

$$\underset{\substack{\text{(concentrated}\\\text{nitric acid)}}}{4\ HNO_3} + C \longrightarrow 4\ NO_2\uparrow + CO_2\uparrow + 2\ H_2O$$

Nitric acid oxidizes certain organic substances, such as hair, wool, vegetable fibres and indigo. It oxidizes flesh, and so great care must be used in handling nitric acid. Proteins are changed by nitric acid to a yellow compound, which changes to an orange colour on the addition of ammonium hydroxide. This is known as the *xantho-proteic reaction* and it is a good test for nitric acid. Cellulose, the chief component of cotton and wood, reacts with nitric acid to give *cellulose nitrate.* This material is used in the manufacture of many useful products, such as explosives and artificial leather. Glycerine, when treated with nitric acid, forms *nitro-glycerine*, glyceryl tri-nitrate, which is the basic explosive material in dynamite.

$$\underset{\text{(glycerine)}}{C_3H_5(OH)_3} + 3\ HNO_3 \longrightarrow \underset{\text{(nitro-glycerine)}}{C_3H_5(NO_3)_3} + 3\ H_2O$$

When nitric acid acts on toluene, a high explosive, trinitrotoluene, $CH_3.C_6H_2.(NO_2)_3$, commonly known as T.N.T., is formed.

(4) REACTS WITH HYDROCHLORIC ACID TO FORM AQUA REGIA. A mixture, consisting of three parts of hydrochloric acid and one part of nitric acid by weight, will dissolve gold and platinum. This is known as *aqua regia*, which means "royal water," because it dissolves gold, considered by the alchemists to be the most "noble" of all metals. The reaction between the two acids is considered to be as follows:

$$HNO_3 + 3\ HCl \longrightarrow 2\ H_2O + Cl_2 + \underset{\substack{\text{(nitrosyl}\\\text{chloride)}}}{NOCl}$$

The chlorine produced by the above reaction combines with gold and platinum, forming soluble compounds of these metals.

5. The Chemical Test for the Nitrate Ion

The sample believed to contain the nitrate ion is dissolved in water, and then a freshly prepared solution of ferrous sulphate is added to it. These materials are well mixed and placed in a test tube. A small quantity of concentrated sulphuric acid is now poured slowly down the inner wall of the test tube. The formation of a dark brown ring at the juncture of the two liquids, after a few seconds, indicates the presence of the nitrate ion. This dark brown colour is thought to be due to the presence of the complex ion, $FeNO^{++}$.

6. Uses

Nitric acid is used in the manufacture of nearly all *explosives*, such as nitro-glycerine (dynamite), gun-cotton, cordite, and T.N.T.

Many *dyes*, such as the coal tar dyes, require nitric acid in their manufacture.

It is also used in making certain *plastics*, *lacquers*, and *drugs*.

Nitric acid is used in *metallurgical operations* such as the separation of gold from silver. The acid is also used in the *pickling of brass*. Nitric acid is essential for *photo-engraving*. The *production of nitrates*, such as those of copper and silver, requires considerable quantities of the acid. Ammonium nitrate, formed by the action of ammonia and nitric acid, is a very important fertilizer.

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

From the above discussion it is evident that nitric acid plays an important role in chemical industry.

As nitric acid is very difficult to transport, many companies, which use large quantities of it, manufacture their own at those factories where it is going to be used. A mixture of sulphuric and nitric acid, known as "mixed acid," is used considerably in industry. This liquid can be shipped safely in steel tank cars. When the nitric acid is not mixed with sulphuric acid, it must be transported in glass or chrome-iron drums.

EXERCISES

1. (a) Describe the laboratory preparation of nitric acid. Illustrate your answer with a labelled drawing.
   (b) Write the equation for the reaction in (a).

2. Write the equations for reactions taking place in the Ostwald Process.
3. (a) Write the equations for the reactions in the Birkeland-Eyde Process.
   (b) How does nature produce nitric acid, and how is this related to soil fertility?
4. (a) Tabulate four physical properties of nitric acid.
   (b) Tabulate four chemical properties of nitric acid and illustrate each property by means of an equation.
5. Describe the chemical test for the nitrate ion.
6. Tabulate five uses of nitric acid.
7. Write a short note on the transportation of nitric acid.

CHAPTER XL

SODIUM AND ITS CHIEF COMPOUNDS

SODIUM—A TYPICAL METAL

1. Metals and Non-metals

Chemical elements can be classed into two chief types, metals and non-metals. As a rule, a few of the non-metallic elements and their chief compounds are considered first in the study of elementary chemistry. Thus far we have studied the following non-metallic elements and their chief compounds: oxygen, hydrogen, carbon, nitrogen, chlorine, and sulphur. We shall now study some of the more important metallic elements and a few of their chief compounds. Sodium, calcium, iron, and aluminum have been selected for careful consideration because they are typical and important metals.

Metals and non-metals have certain marked physical and chemical differences. Metals possess a characteristic lustre; they are usually malleable (can be hammered or rolled into thin sheets); they are, as a rule, ductile (can be drawn, when heated, into wires or threads); and they are also good conductors of heat and electricity. These are physical properties, very few of which are possessed by non-metals.

Metals are base forming elements; that is, their oxides (basic anhydrides) combine with water to form bases. For example, the metal calcium burns in air to produce calcium oxide, which combines with

$$2\ Ca + O_2 \longrightarrow 2\ CaO$$

water to form calcium hydroxide, a base.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Non-metals, on the other hand, are acid forming elements; that is, their oxides (acidic anhydrides) combine with water to form acids. For example, sulphur burns in air to produce sulphur dioxide, which combines with

$$S + O_2 \longrightarrow SO_2$$

water to form sulphurous acid.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

This difference between metals and non-metals is one of the chief chemical differences between these two types of elements.

Another chemical difference between metals and non-metals is the tendency of their atoms to gain or lose electrons. The atoms of a metallic element tend to lose electrons to form positive ions. Thus, a sodium atom loses one electron very readily from its outermost orbit to form a positive sodium ion.

$$\underset{\text{(sodium atom)}}{\mathrm{Na}^{\circ}} \xrightarrow{(-\text{ 1 electron})} \underset{\text{(sodium ion)}}{\mathrm{Na}^{+}}$$

Atoms of the active metals, such as sodium and potassium, lose electrons very readily. On the other hand, atoms of the inactive metals, such as platinum and gold, do not lose their electrons readily. The atoms of non-metallic elements tend to gain electrons to form negative ions. Thus, a chlorine atom gains one electron quite readily to complete its outermost orbit, forming a negative chlorine ion.

$$\underset{\text{(chlorine atom)}}{\mathrm{Cl}^{\circ}} \xrightarrow{(+\text{ 1 electron})} \underset{\text{(chlorine ion)}}{\mathrm{Cl}^{-}}$$

Atoms of the active non-metals, such as fluorine and chlorine, gain electrons very readily. Less active non-metals, such as iodine, do not gain electrons readily.

2. Metallurgy

Metallurgy is the science of extracting metals from their ores. A *mineral* is a naturally occurring chemical compound in whose formation the life processes of a living thing have played no part. An *ore*, on the other hand, is a mineral which can be profitably treated to extract a metal.

Most metals are found in nature combined with non-metallic elements as oxides, sulphides, carbonates, silicates and other compounds. Sometimes the metal is found free in nature as in the case of gold. The minerals containing the metal, however, often make up only a very small fraction of the ore which is taken from the mine. For example, some gold ores contain only a few ounces of the precious metal per ton. The ore, therefore, must be treated by two separate processes before the metal is obtained from it. The first process consists of removing the waste rock, known as *gangue*, from the useful mineral. This process is called *ore-dressing* or *concentration*. The second process consists of treating the mineral, obtained by the first process, in such a way as to remove the metal from the oxygen, sulphur, or whatever constituents it is combined with in the mineral.

This second process is called *metallurgy*. All the operations taking place in the mine until the ore is carried to the surface in elevators is called *mining*. Details of ore-dressing or mining cannot be given in this book but the metallurgy of several important metals will be given in some detail.

3. Occurrence of Sodium

Free sodium does not occur in nature because of its great chemical activity. Some of its compounds, however, are quite familiar to most people, and they occur abundantly in nature. The chief source of sodium and its compounds is common salt, sodium chloride, NaCl. Large quantities of sodium are found combined with silicon and other elements in certain rocks, such as the mineral *albite*, $NaAlSi_3O_8$. These rocks are decomposed by the weather into simpler compounds. Some of these compounds contain sodium, and as all common sodium compounds are soluble in water, most of the sodium is washed out of the soil. This means that, in time, many sodium compounds find their way to the ocean. Several important deposits of sodium compounds are found in desert regions. Thus, rich deposits of *sodium nitrate* ($NaNO_3$) are found in Chile, and so this compound is often called *Chile saltpetre*. *Sodium carbonate* (Na_2CO_3) is found in nature as the mineral *trona*, in Egypt, California, and in several other localities. Sodium tetraborate, known commonly as borax ($Na_2B_4O_7$) occurs in the Death Valley area of southern California.

4. Production of Sodium

Sodium was first prepared in 1807 by the English chemist, Sir Humphry Davy, by passing an electric current through fused (melted) sodium hydroxide. He also discovered the metal potassium at the same time by the electrolysis of fused potassium hydroxide.

Metallic sodium is still produced in industry by the same method, which was developed into a technical process by Castner in England. A diagram of the Castner cell is shown in Fig. 154. The outside vessel consists of iron. The heat needed to change the sodium hydroxide to the molten state is produced by the resistance of the hydroxide to the flow of the electric current. The sodium hydroxide in the lowest part of the container stays in the solid state and aids in holding up the cathode, which is an iron bar. The anode consists of several bars of nickel, held in position from the top of the cell. Around the cathode is a diaphragm made of wire gauze, which extends quite far above the molten sodium hydroxide (caustic soda) and ends in an iron cylinder. The purpose of this gauze is to keep separated the products formed at the two electrodes. The heat produced by the resistance of the liquid to the flow of electric current is increased by gas flames playing against the bottom of the cell. Sodium and hydrogen are produced at the cathode. The sodium is in the liquid state and, since it is lighter than the molten caustic soda (NaOH), floats to the top. It is prevented from being oxidized by the oxygen of the air by the hydrogen formed along with the metal. The molten sodium is removed from time to time by a gauze ladle. The equation for the reaction is:

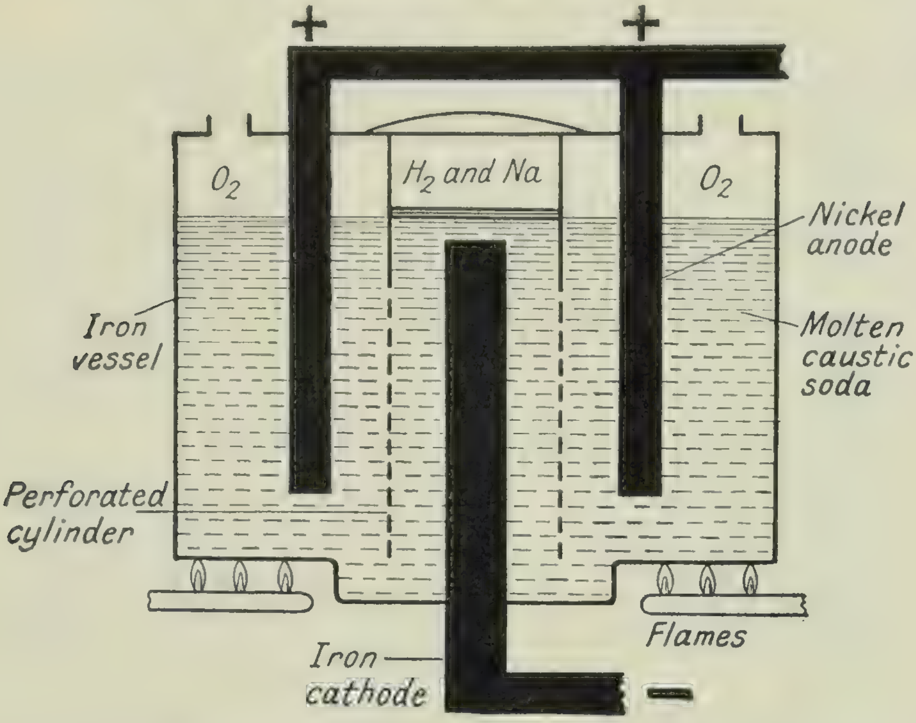


FIG. 154—MANUFACTURE OF SODIUM BY THE CASTNER PROCESS

$$2\ \mathrm{NaOH} \longrightarrow 2\ \mathrm{Na} + \mathrm{H_2}\uparrow + \mathrm{O_2}\uparrow$$

Metallic potassium can be produced in exactly the same way.

Recently sodium hydroxide cells have been replaced to a very large extent by sodium chloride cells, known as Downs cells, which produce chlorine along with metallic sodium (See Fig. 155). The equation for the reaction is:

$$2\ \mathrm{NaCl} \longrightarrow 2\ \mathrm{Na} + \mathrm{Cl_2}\uparrow$$

Sodium is set free on the surface of the iron cathodes and rises to the top through the compartment which surrounds the cathodes.

The anode is made of graphite and it is separated from the cathodes by gauze diaphragms. At the temperature (600°C.) at which the electrolysis takes place the sodium remains in the liquid state, and so it overflows from the cathode compartment into a container where it is collected under oil. Chlorine collects around the anode and escapes through an opening at the top of the apparatus.

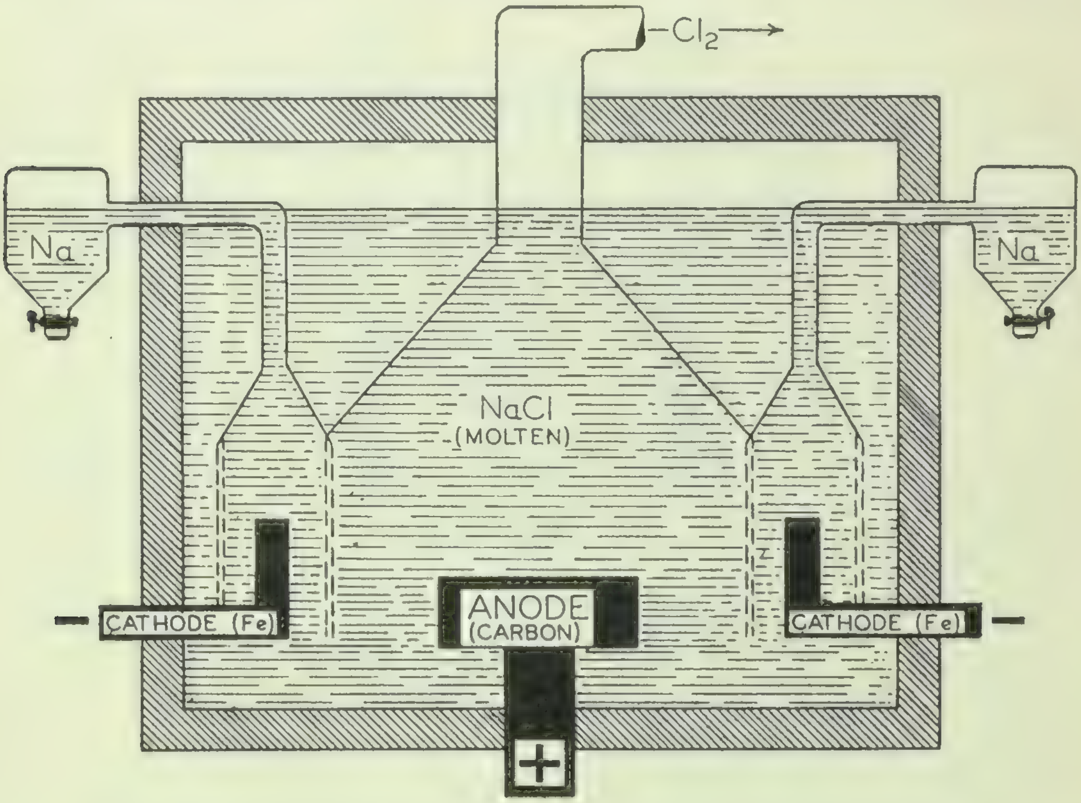


FIG. 155—THE MANUFACTURE OF SODIUM BY THE DOWNS CELL

5. Properties of Sodium

(1) PHYSICAL PROPERTIES. (a) Sodium is a soft *solid*, which can be cut with a knife.

(b) It has a *silvery lustre* when freshly cut.

(c) The metal is slightly *lighter than water*; its specific gravity is 0.97.

(d) Sodium, like most metals, is *malleable.*

(e) It is *ductile* and so can be drawn out into a wire.

(f) The metal is a *conductor of heat and electricity.*

(g) Sodium melts at 98°C., and so boiling water would change it to the liquid state.

(2) CHEMICAL PROPERTIES. (a) *Sodium burns in oxygen or air* to form sodium peroxide.

$$2\ Na + O_2 \longrightarrow \underset{\text{(sodium peroxide)}}{Na_2O_2}$$

The metal or any of its compounds gives a bright yellow colour to a non-luminous Bunsen flame. This is used as a test for the metal or its ion.

(b) *It reacts vigorously with water* producing sodium hydroxide and hydrogen.

$$2\ Na + 2\ H_2O \longrightarrow 2\ NaOH + H_2\uparrow$$

(c) *The metal reacts with chlorine,* forming sodium chloride (common salt). It also reacts in the same way with the other halogens.

$$2\ Na + Cl_2 \longrightarrow 2\ NaCl$$

(d) Sodium is an excellent *reducing agent.*

6. Uses of Sodium

Sodium, with a purity of 99.9%, is produced commercially today, and it is used to make compounds of the element which cannot be produced readily from sodium chloride.

Some of the chief uses are as follows:

(1) *To make sodium cyanide* (NaCN), which is used in electroplating, case-hardening of steel, fumigation, extraction of gold from its ores, and in the manufacture of certain dyes.

(2) *To make sodium peroxide,* which is used to a considerable extent in the bleaching of certain textiles.

(3) *In the synthesis of indigo.* Sodium is needed to make artificial indigo, which is an important dye.

(4) Sodium is also used in the manufacture of certain *detonators.*

(5) *Sodium vapour lamps* find certain important uses. For example, at large airports they are often used to assist the landing of planes during a dense fog. These lamps are visible for a distance of 410 feet in fogs, whereas ordinary electric lights are visible for a distance of only 33 feet under the same weather conditions.

(6) Sodium is used to produce *lead tetraethyl,* an organic compound used as an anti-knock material in gasoline. This substance is made by the reaction of ethyl chloride, C_2H_5Cl, with an alloy of sodium and lead.

Sodium is kept in the laboratory under an oil such as kerosene. It is shipped in large quantities in sealed tank cars. Of course, air and moisture must be carefully kept out of the car. The metal is taken out of the car by melting it. This is done by passing hot oil through pipes which are built into the car. The liquid sodium is then removed by suction in an atmosphere of nitrogen. These special tank cars carry as much as 40 tons of the metal.

SODIUM CHLORIDE

1. Occurrence

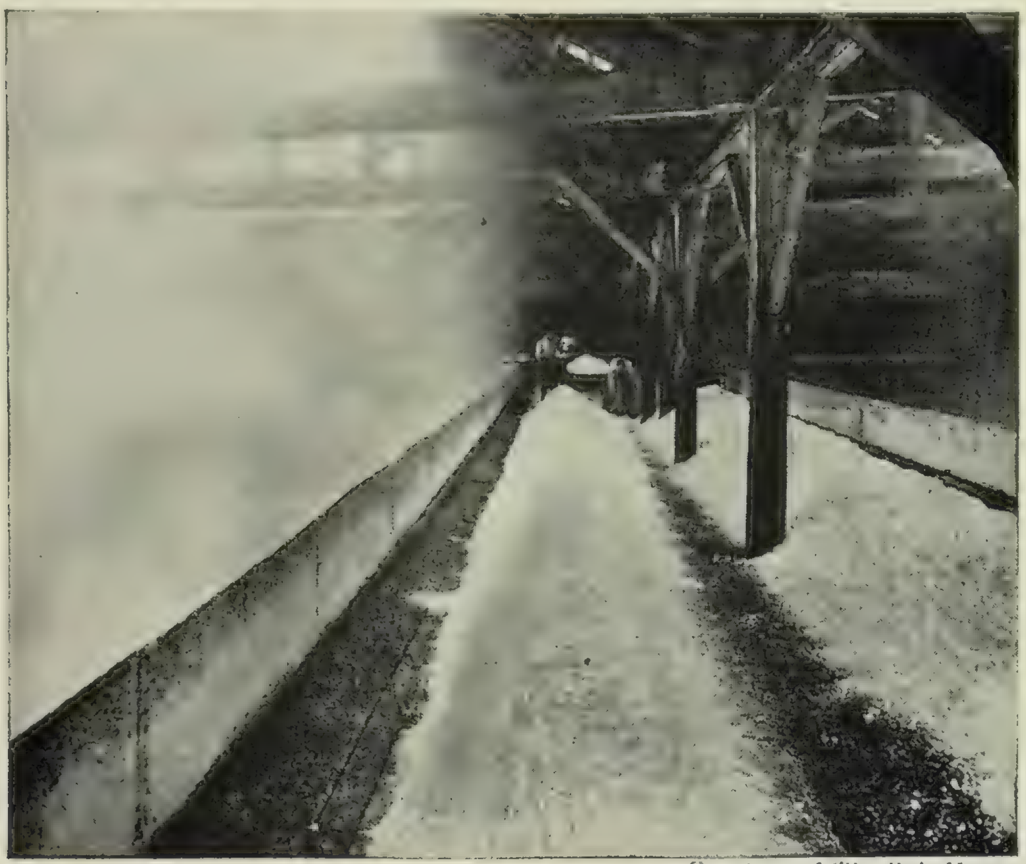
Sodium chloride, NaCl, common table salt, is one of the most abundant and important compounds used by man. Salt is readily soluble in water, and so occurs in brine springs in almost every country. It occurs in ocean water to the extent of about 3 per cent. The water of the Dead Sea and of Great Salt Lake has about 20 per cent sodium chloride in it. Deposits of salt are found in different parts of the earth. For example, huge deposits of salt are found near Stassfurt, Germany. Numerous rich deposits of salt are found in the United States.

Canada is fortunate in having enormous quantities of salt in various forms, such as salt seepages, brine springs, saline lakes, salt marshes and, more rarely, underground deposits of rock salt, from one end of the country to the other. Most of these salt deposits have no present commercial value. Our salt industry is chiefly located in one area, along the Detroit River and the south shore of Lake Huron. However, there has been some development of salt mining in Nova Scotia and recovery from natural brine in Manitoba and Alberta. Recent calculations show that the salt beds of Ontario contain enough of the mineral to supply the world's needs for at least 90,000 years.

2. The Refining of Salt

The production of salt consists chiefly of three physical changes: solution, evaporation, and crystallization. Most of the salt used in Canada is obtained from deposits which are more than a quarter of a mile underground. For example, at a modern salt plant at Windsor, Ontario, wells are driven into "deep salt," hundreds of feet below the earth's surface; the drill keeps on until it reaches the bottom of the bed, usually at about 1,600 feet. Each well casing consists of two pipes, one inside the other. Water, under a pressure of 175 pounds to the square inch, is forced down the larger, outer pipe. The water dissolves the rock salt, and the brine (salt solution) is forced up the smaller, inner pipe. The brine is poured into huge tanks, each thousands of gallons in capacity, where insoluble substances settle to the bottom. The brine is purified by chemical treatment, filtered, and then pumped to the evaporators.

There are two chief methods for treating the purified brine, and the form in which the salt is desired determines which process shall be used. Large crystals of coarse salt, or the flat flakes of flake salt, are produced by the open evaporator, or grainer process, as shown in Fig. 156. Fine salt is produced in the vacuum evaporator process. Both processes are used in most Canadian salt plants.

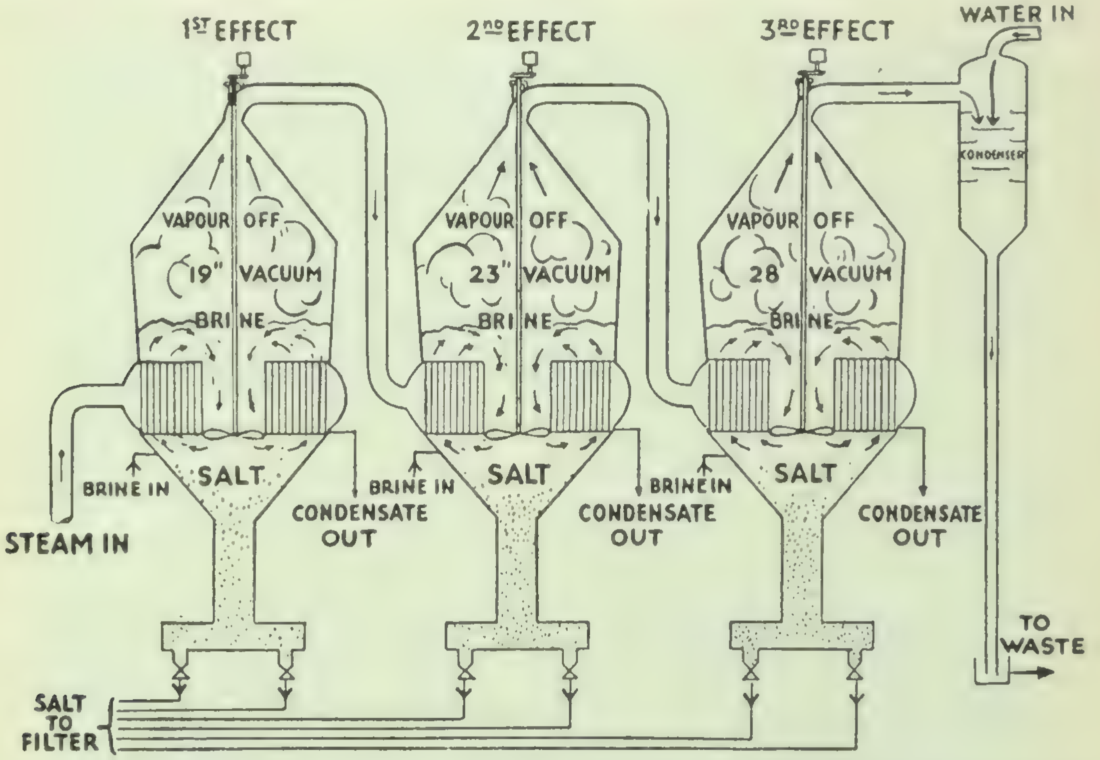


Courtesy of The Salt Union

FIG. 156—SALT OBTAINED FROM SALT PANS BY EVAPORATION

The vacuum evaporator process is the modern method of producing salt, and it is much more efficient than the open evaporator. The temperature at which any liquid boils depends upon two things; first, the nature of the liquid, and secondly, the pressure of the air above it. Water boils at a lower temperature on mountain tops than at sea level because the pressure of the atmosphere is less at higher levels. If some of the air is removed from a closed container partly filled with water, and if the water vapour is removed as fast as it is formed, then the boiling point of the liquid will be lowered to a marked degree. This is what takes place in vacuum evaporators.

Let us now consider how the vacuum evaporators, sometimes known as pans, operate. A diagrammatic sketch of the process is shown in Fig. 157. Live steam is passed into the steam chamber of the first pan where the brine starts to boil. The steam, given off by the boiling brine, passes to the steam chamber of the second pan, where the brine surrounding it is comparatively cool. Thus, the steam condenses at once and gives up its heat to the brine in the second pan. This condensation of the steam produces a partial vacuum in the first pan, and so the brine there will boil more vigorously. In a short time the brine in the second pan commences to boil, and the steam formed passes on to the steam belt of the third evaporator. Here the steam condenses and heats the brine, producing a partial vacuum in the second pan. A stream of cold water, falling through the ejector or vacuum pump attached to the third pan, condenses the steam drawn off by the pump. This produces and keeps a high vacuum in the third evaporator, so that the brine there soon starts to boil at a fairly low temperature. Thus, the salt solutions in all three evaporators are vigorously boiled with the heat which was originally supplied to the first pan. Crystallized salt descends in a steady stream to the bottom of each evaporator. It is then dried in a current of hot air, and screened.



Courtesy of Canadian Industries Limited

Fig. 157—A Diagrammatic Representation of Triple Effect Vacuum Pan Evaporators in a Modern Salt Plant. The Two Small Shaded Squares in the Centre of Each Evaporator are the "Steam Belts"

The screening process grades the salt according to the size of the crystals. The finest grade is used for table salt and the larger sized crystals are used for other purposes.

3. Properties of Salt

(1) Sodium chloride is a white solid, which crystallizes in cubes.
(2) Salt crystals do not contain water of crystallization, but, as a rule, they have water which is mechanically enclosed by the crystal. When a salt solution is being evaporated to dryness, this enclosed water brings about an explosion of the crystals with a crackling sound. This phenomenon is known as *decrepitation.*
(3) It has a "salty" taste which is similar to that possessed by most salts.
(4) Salt is quite soluble in water, 35.7 grams dissolving in 100 grams of water at 0° C. and only 39.8 grams at 100° C. This is rather unusual as most solids are much more soluble in hot water than in cold.
(5) Pure sodium chloride is not deliquescent. Common table salt, however, does show this property, because it contains, as an impurity, very small quantities of magnesium chloride which is deliquescent.

4. Uses of Salt

(1) *Salt is an essential food.* It is said to supply the body almost entirely with hydrochloric acid, an important part of the digestive juice.
(2) It is used as a *preservative* for meat, fish and other foods.
(3) Sodium chloride is one of the most essential raw materials of the *chemical industry.* It is the starting material for the production of several important industrial chemicals, such as sodium hydroxide, sodium carbonate, sodium bicarbonate, hydrochloric acid, sodium hypochlorite, and chlorine.

SODIUM HYDROXIDE (A Typical Base)

1. Preparation

(1) BY THE ACTION OF SODIUM CARBONATE WITH SLAKED LIME.

$$\underset{\substack{\text{sodium}\\ \text{carbonate}\\ \text{(washing soda)}}}{Na_2CO_3} + \underset{\substack{\text{calcium}\\ \text{hydroxide}\\ \text{(slaked lime)}}}{Ca(OH)_2} \longrightarrow CaCO_3\downarrow + 2\ NaOH$$

In this method the insoluble calcium carbonate is removed by filtration and sodium hydroxide (caustic soda) is obtained by evaporation of the filtrate. This is the oldest commercial method of making sodium hydroxide and it is still used to a considerable extent.

(2) By the Electrolysis of a Common Salt Solution. According to the Ionic Theory sodium chloride ionizes in water as follows:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Water ionizes to a very limited extent as follows:

$$H_2O \rightleftharpoons H^+ + OH^-$$

These ideas are reviewed because they are needed to explain the reactions which take place when the electric current is passed through a solution of sodium chloride. When a direct current is passed through a common salt solution, the positive sodium and hydrogen ions are attracted towards the cathode (negative) as shown in Fig. 158. It requires less electrical energy to discharge the hydrogen ions than it does to discharge the sodium ions. Thus, the hydrogen ions are changed to hydrogen atoms, which in turn form hydrogen molecules by the process of sharing one pair of electrons. The equations for the reaction at the cathode are given below.

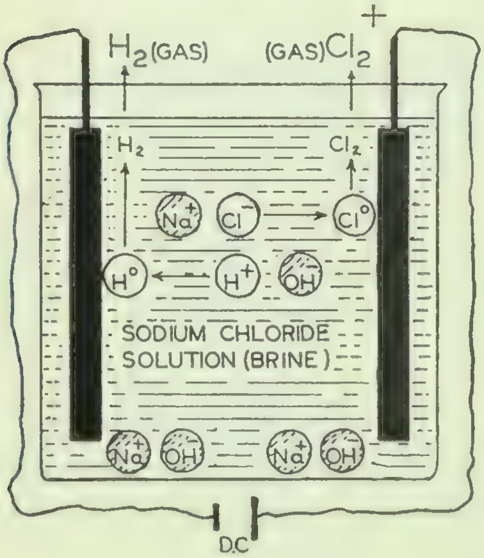


Fig. 158

Explanation of Electrolysis of a Common Salt Solution by Means of the Ionic Theory

$$\underset{\text{(ion)}}{H^+} + 1\text{ electron} \longrightarrow \underset{\text{(atom)}}{H^\circ}$$

$$2\,H^\circ \xrightarrow[\text{of electrons}]{\text{share one pair}} \underset{\text{(a molecule)}}{H_2}$$

Millions of the hydrogen molecules, because of molecular attraction, form bubbles of the gas. These escape around the cathode. As long as the current is kept at a low voltage, the hydrogen ions are discharged as explained above and the sodium ions remain in solution.

The negative chloride and hydroxyl ions are attracted to the anode (positive) as shown in Fig. 158. In this case it takes less electrical energy to discharge the chloride ions than it does to discharge the hydroxyl ions. Thus, the chloride ion loses one electron when it reaches the anode, and so it is converted into a chlorine atom. Two chlorine atoms combine, by the sharing of a pair of electrons, to form a chlorine molecule. Millions of these molecules are held together, by molecular attraction, to form bubbles of chlorine gas, which escape around the anode. The equations for the reactions at the anode are given below.

$$\underset{\text{(ion)}}{Cl^-} \xrightarrow{\text{(— 1 electron)}} \underset{\text{(atom)}}{Cl^\circ}$$

$$\underset{\text{(atoms)}}{2\ Cl^\circ} \xrightarrow[\text{of electrons}]{\text{share 1 pair}} \underset{\text{(molecule)}}{Cl_2}$$

Much of the chlorine produced in industry is obtained by the electrolysis of a concentrated common salt solution. There are various methods of doing this but we shall only describe one,

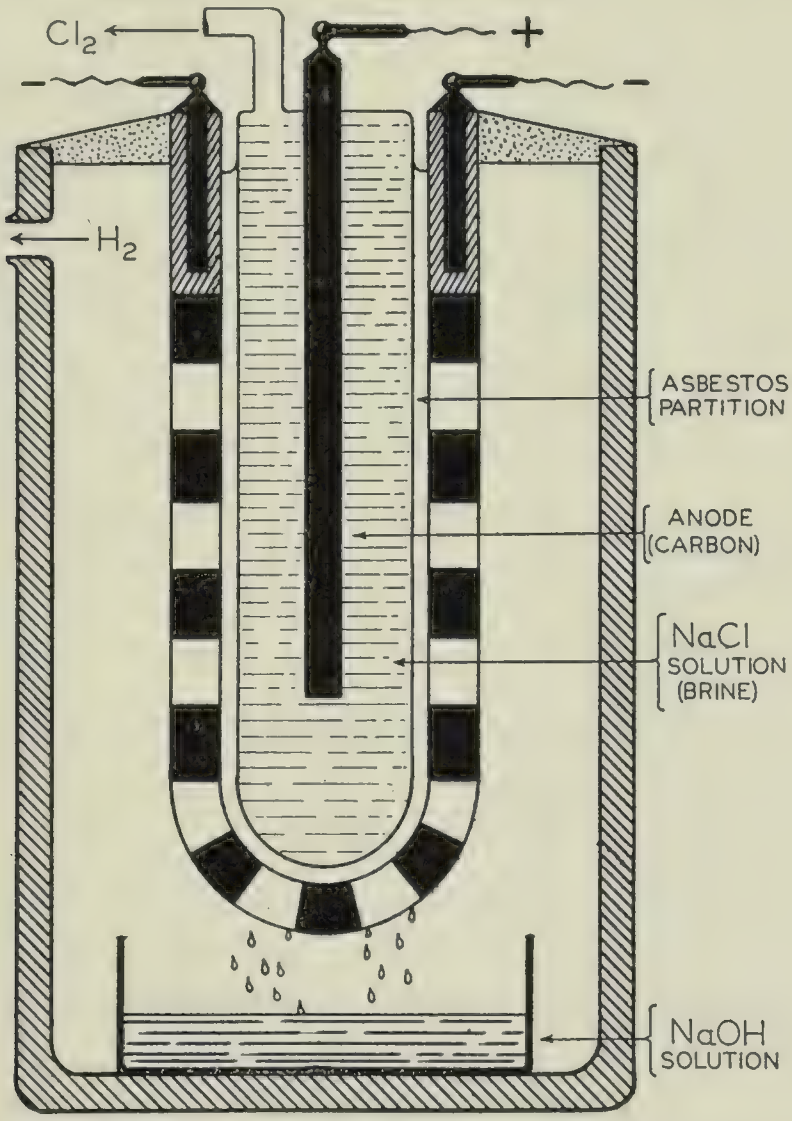


FIG. 159—THE NELSON CELL FOR THE ELECTROLYSIS OF SODIUM CHLORIDE SOLUTION (BRINE)

which is used to a marked extent. This method uses an electrolysis device, known as the Nelson cell. A diagram of this apparatus is shown in Fig. 159. This cell consists of two main parts, an inner chamber and an outer compartment. The outer walls of the cell are constructed of slate. The anode, consisting of graphite, is held in position in the inside compartment from the cover of the slate container. The inner vessel is made of iron and it holds the concentrated solution of sodium chloride (brine). It serves as the cathode. The walls of this container have a number of small openings and are lined with an asbestos diaphragm. When the current is turned on, chlorine collects around the anode (positive) and escapes through an outlet in the slate box. The anode is made of graphite and the outer container of slate because chlorine does not react with these substances. The sodium chloride solution drips through the diaphragm slowly, and so meets the perforated iron cathode. The hydrogen ions are discharged and converted into gaseous hydrogen, which escapes from the outer chamber through an opening in the top of the cell. The sodium ions, not being discharged, and accompanied by hydroxyl ions, pass through the openings in the cathode, and so a solution of sodium hydroxide is collected at the bottom of the outer compartment, from which it is drained away. It should be remembered that the asbestos diaphragm prevents the chlorine from coming into contact with sodium hydroxide and so reacting to form sodium hypochlorite (NaClO).

$$2\,NaOH + Cl_2 \longrightarrow NaClO + NaCl + H_2O$$

2. Physical Properties of Sodium Hydroxide

(1) Sodium hydroxide is a white solid.

(2) It is very soluble in water.

(3) This solid is extremely deliquescent, taking up much water from the air when left exposed to it.

(4) Caustic soda has a soapy feeling.

3. Chemical Properties of Sodium Hydroxide

(1) This substance forms a *strong base* when placed in water because it ionizes almost completely as follows:

$$NaOH \rightleftharpoons Na^+ + OH^-$$

Thus, a solution of this base in water would turn red litmus blue, and it would also neutralize acids. For example, it neutralizes hydrochloric acid to form sodium chloride and water.

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

(2) Sodium hydroxide is a very *corrosive* substance, and for that reason is known in commerce as caustic soda. It attacks the *skin* and *flesh* readily, and it also dissolves *silk* and *wool.*
(3) Caustic Soda reacts with vegetable and animal fats to produce soaps. A simple equation for this process is:

Fat + lye (NaOH) ⟶ Soap + Glycerine.

(4) Sodium hydroxide reacts with carbon dioxide to form sodium carbonate, commonly known as washing soda.

$$2\ NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

4. Uses of Sodium Hydroxide

(1) One of the chief industrial uses of sodium hydroxide is its use in *soap manufacture.*
(2) Large quantities of it are also used in *refining petroleum.*
(3) It is also used in the *manufacture of paper.*
(4) Sodium hydroxide is used in *making rayon* by the "viscose" process.
(5) Caustic soda is sold as *lye* for household use because a strong solution of this substance readily dissolves grease. It is, therefore, used to clean sinks and enamelware.

SODIUM CARBONATE

1. Preparation

Sodium carbonate (Na_2CO_3), commonly known as washing soda, is prepared today chiefly by the *Solvay Process.* The steps in this process are:

1. Carbonate dioxide is produced by heating limestone ($CaCO_3$).

$$CaCO_3 \longrightarrow CaO + CO_2\uparrow$$

2. Ammonia and carbon dioxide are passed, under pressure, into a saturated solution of common salt. The reactions which occur are represented by the following equations.

(1) $NH_3 + H_2O \longrightarrow NH_4OH$

(2) $CO_2 + H_2O \longrightarrow H_2CO_3$

(3) $NH_4OH + H_2CO_3 \longrightarrow NH_4HCO_3 + H_2O$

(4) $NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$

These reactions can be summarized in one equation as follows:

$$NaCl + H_2O + NH_3 + CO_2 \longrightarrow NaHCO_3 + NH_4Cl$$

3. The sodium bicarbonate, $NaHCO_3$, is only slightly soluble in the solution in which it is formed, and so the reaction goes to completion because that substance is precipitated.

4. The sodium bicarbonate is then changed into sodium carbonate by heating it.

(5) $2\ NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2\uparrow$

5. Ammonia is recovered from the ammonium chloride, produced in reaction (4), by heating the chloride with the quicklime, formed on heating the limestone in the first step of the process.

$$CaO + 2\ NH_4Cl \longrightarrow CaCl_2 + H_2O + 2\ NH_3\uparrow$$

2. Properties

(1) When a solution of sodium carbonate is evaporated to dryness slowly, the residue consists of large transparent crystals, which on analysis are found to have the formula $Na_2CO_3 . 10H_2O$. This material is commonly called washing soda. The crystals of this substance lose their water of crystallization on exposure to the air and crumble to a white powder. This phenomenon is called *efflorescence.* The anhydrous sodium carbonate is known as *soda ash.*

(2) Sodium carbonate in solution gives a *basic reaction.* This is due to slight hydrolysis of the sodium carbonate by the water. The reaction can be expressed thus:

$$Na_2CO_3 + 2\ HOH \longrightarrow 2\ NaOH + H_2CO_3$$

(3) It has all the properties of a typical carbonate. For example, it reacts with hydrochloric acid to form carbon dioxide

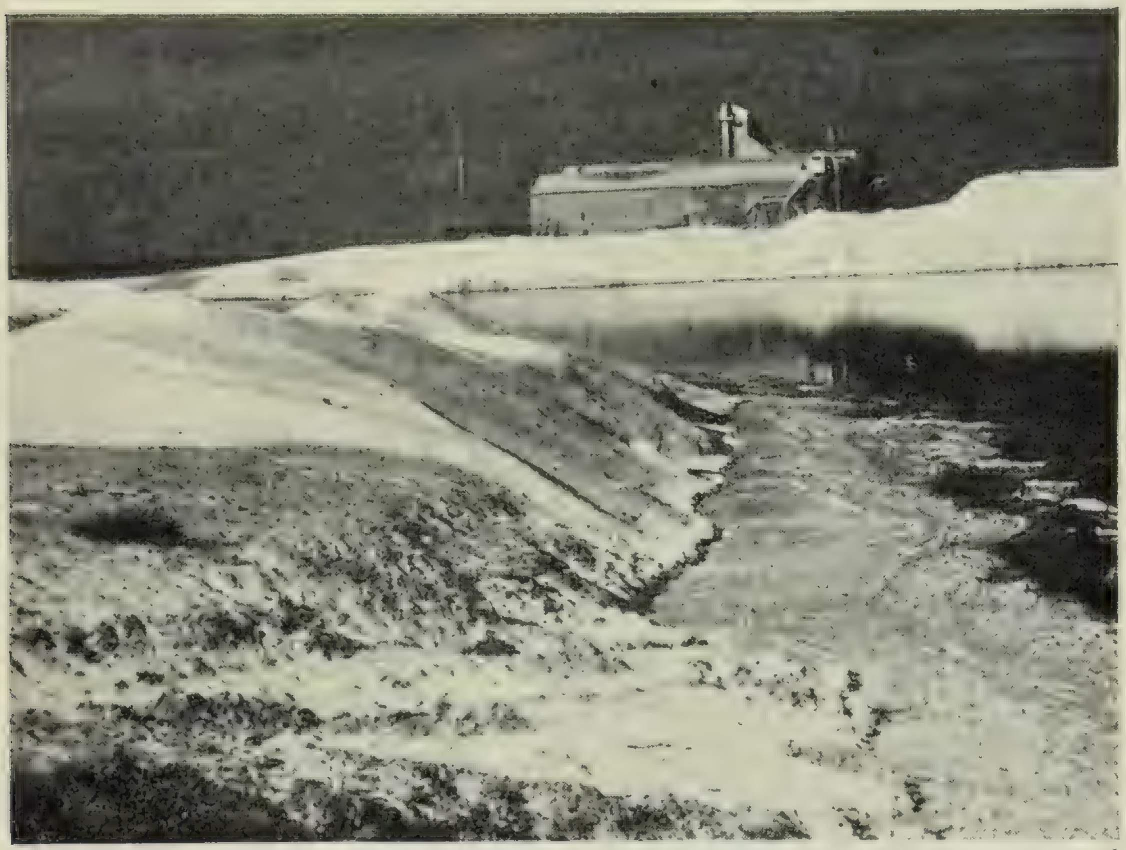
$$Na_2CO_3 + 2\ HCl \longrightarrow 2\ NaCl + H_2O + CO_2\uparrow$$

3. Uses

Sodium carbonate is a very important industrial chemical. It is used in the manufacture of glass, soap, and soap powders. It is also used a great deal to soften water. Sodium carbonate is needed in refining petroleum, in the manufacture of sodium hydroxide, in the paper industry, and for the production of many important chemicals.

SODIUM SULPHATE

Sodium sulphate, $Na_2SO_4 . 10H_2O$, sometimes called *Glauber's salt,* is found in large quantities in "lakes" located in certain parts of Western Canada. A very rich deposit was discovered some years ago in White Shore Lake, near Palo, situated about 70 miles west of Saskatoon, Saskatchewan. It was estimated that this deposit contained approximately 20,000,000 tons of hydrated sodium sulphate. At the present time a thriving industry is located there and thousands of tons of sodium sulphate are shipped each year. Several other sodium sulphate refining plants are in operation at various places in Saskatchewan.



Courtesy of Canadian Industries, Ltd.

Fig. 160—Piles of Sodium Sulphate, Obtained from Natural Deposits in White Shore Lake, near Palo, Saskatchewan

Tens of thousands of tons of the dehydrated crystal, known in commerce as "salt cake," are needed each year in the manufacture of kraft paper by the sulphate process. The fibre of the paper obtained by the sulphate process has unusual strength and flexibility. The glass industry also uses sodium sulphate to lower the melting point and viscosity of the liquid glass. Much salt cake is used in the smelting of nickel and copper ores. It is also used in the production of certain chemicals.

EXERCISES

1. Discuss the physical and chemical differences between metals and non-metals.
2. Define the following: metal, non-metal, metallurgy, mineral, ore, gangue, ore-dressing, mining.
3. Write a note on the occurrence of sodium.
4. Describe briefly the Castner process of producing metallic sodium. Illustrate your answer with a labelled diagram.
5. Describe briefly the Downs cell for the production of metallic sodium: Illustrate your answer with a labelled diagram.
6. Tabulate five physical properties of sodium.
7. Tabulate three chemical properties of sodium and illustrate each by means of an equation.
8. Tabulate five uses of sodium.
9. Write a short note on the occurrence of sodium chloride.
10. (a) What are the three chief physical changes which occur in the refining of salt?
    (b) Discuss briefly the method of extracting salt from underground deposits.
    (c) What are the two chief methods for treating the purified brine?
    (d) Describe briefly the vacuum evaporator process.
11. (a) Tabulate five properties of salt.
    (b) Tabulate three uses of salt.
12. (a) Discuss the preparation of sodium hydroxide by means of the electrolysis of a common salt solution. Illustrate your answer by means of a labelled diagram.
    (b) Write ionic equations for the reactions which take place at each electrode.
    (c) Make a labelled diagram of a Nelson cell. Describe briefly how this cell works.
13. (a) Tabulate four physical properties of sodium hydroxide.
    (b) Tabulate four chemical properties of sodium hydroxide.
    (c) Tabulate five uses of caustic soda.
14. Write molecular equations to show the steps in the Solvay process.
15. (a) Tabulate three properties of sodium carbonate.
    (b) Tabulate five uses of sodium carbonate.
16. Discuss sodium sulphate under: (a) occurrence; (b) uses.

CHAPTER XLI

CALCIUM AND ITS CHIEF COMPOUNDS

CALCIUM

1. Occurrence

Calcium does not occur in nature in the free state. However, its compounds are very abundant in nature. Calcium carbonate, $CaCO_3$, in the form of *limestone* and *marble*, is found in huge quantities in nature. Other calcium compounds found in nature are the hydrated calcium sulphate, $CaSO_4 . 2H_2O$, *gypsum;* the fluoride, CaF_2, *fluorspar;* phosphate rock, $Ca_3(PO_4)_2$, and *dolomite*, $CaCO_3 . MgCO_3$. *Bones* and *teeth* contain a high percentage of calcium in the form of calcium phosphate, $Ca_3(PO_4)_2$.

2. Preparation

Calcium is usually prepared by the electrolysis of fused (molten) calcium chloride ($CaCl_2$). The chloride is melted in a graphite container, which is the anode as shown in Fig. 161. The cathode is made of iron and, at the beginning of the electrolysis, it just dips below the surface of the molten electrolyte. However, as time goes on, the cathode is gradually raised as the calcium deposits on it and changes to a solid, the metal itself acting as the cathode.

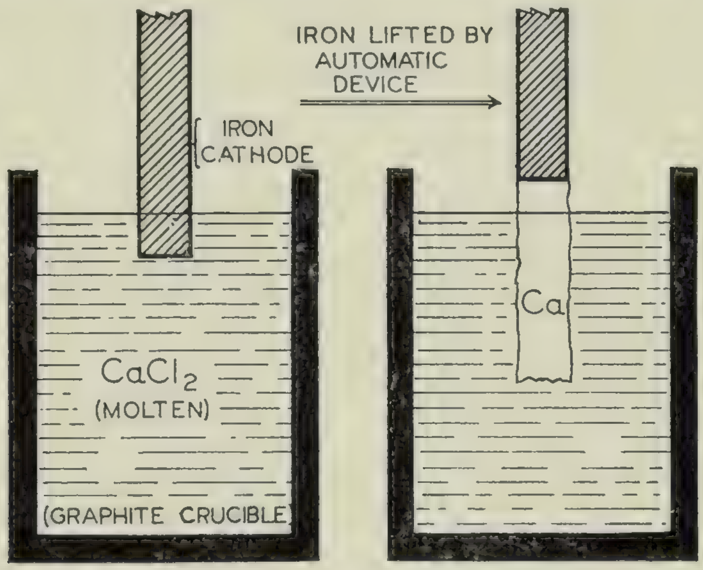


FIG. 161—THE PREPARATION OF METALLIC CALCIUM BY THE ELECTROLYSIS OF FUSED (MOLTEN) CALCIUM CHLORIDE

3. Properties and Uses

(1) Physical. (a) Calcium is a white, silvery metal, but because it enters readily into chemical combination with both oxygen and nitrogen, it tarnishes to form a gray and slightly yellow surface.

(b) It is malleable and ductile.

(c) The metal is heavier than water, having a density of 1.55.

(d) Calcium metal, or its ions, gives an orange-red colour to a non-luminous Bunsen burner flame.

(2) Chemical. (a) Calcium *resists oxidation in dry air*, and so no special care is needed in its storage, except to make sure that moisture is kept away from it.

(b) It *burns very brilliantly* at high temperatures, producing the oxide (CaO) and the yellow nitride (Ca_3N_2).

$$2\ Ca + O_2 \longrightarrow 2\ CaO$$
$$3\ Ca + N_2 \longrightarrow Ca_3N_2$$

(c) The hot metal combines with hydrogen to form a solid, *calcium hydride.*

$$Ca + H_2 \longrightarrow CaH_2$$

This substance reacts with water to produce hydrogen, a convenient but rather expensive method of preparing this gas.

$$CaH_2 + 2\ HOH \longrightarrow Ca(OH)_2 + 2\ H_2\uparrow$$

(d) It reacts with most of the *non-metals* when heated.

$$Ca + Cl_2 \longrightarrow CaCl_2$$

(e) Calcium is a good *reducing agent.*

(f) The metal *reacts readily with water* in the same way as does sodium, but the action is not so vigorous.

$$Ca + 2\ HOH \longrightarrow Ca(OH)_2 + H_2\uparrow$$

(3) Uses. This metal is produced in large quantities because its uses are increasing in number. A few of these uses are given below.

(a) Calcium and barium are mixed with lead to form *bearing-metal alloys.*

(b) It is used to a limited extent as a *reducing agent.*

(c) The metal is used as a *drying and purifying agent* in the manufacture of drugs used to fight certain diseases.

(d) Calcium is used *to deoxidize* (remove oxygen from) copper and its alloys.

(e) It is used in refining certain alloy steels, giving them greater tensile strength.

CALCIUM CARBONATE

1. Occurrence

Calcium carbonate, $CaCO_3$, is the most abundant calcium compound found in nature. It occurs in large quantities in the form of *limestone*. *White marble* is another variety of calcium carbonate which is found in abundance in certain parts of the world. *Iceland spar* (calcite) is a crystalline form of almost pure calcium carbonate and it shows the property of double refraction. Chalk is another form of calcium carbonate found in large amounts in certain places. For example, the famous chalk cliffs of Dover are composed chiefly of calcium carbonate. It is interesting to know that most marine *shells*, as well as such substances as *coral*, *pearls*, and *egg shells*, consist of calcium carbonate. The mineral dolomite is a mixture of calcium and magnesium carbonates, and whole mountain ranges sometimes consist chiefly of this material.

Sometimes a very pure and finely divided calcium carbonate is required for certain uses in industry. It is made by bubbling carbon dioxide into a suspension of calcium hydroxide.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow + H_2O$$

The precipitated product is often known as "precipitated" chalk.

2. Properties

(1) Pure calcium carbonate is a *white solid.*

(2) It is *insoluble in water*, otherwise the marble ruins of ancient Greece would have been washed away many years ago.

(3) Calcium carbonate, like all carbonates, reacts *readily with acids* producing carbon dioxide. This is the usual laboratory method of preparing carbon dioxide.

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2CO_3$$
$$H_2CO_3 \longrightarrow H_2O + CO_2\uparrow$$

(4) *It dissolves in carbonic acid*, being changed to the bicarbonate which is soluble in water.

$$CaCO_3 + H_2CO_3 \longrightarrow \underset{\text{(calcium bicarbonate)}}{Ca(HCO_3)_2}$$

When a clear solution of the bicarbonate is heated, a fine white precipitate of calcium carbonate is formed and carbon dioxide is evolved. The equation for this reaction is:

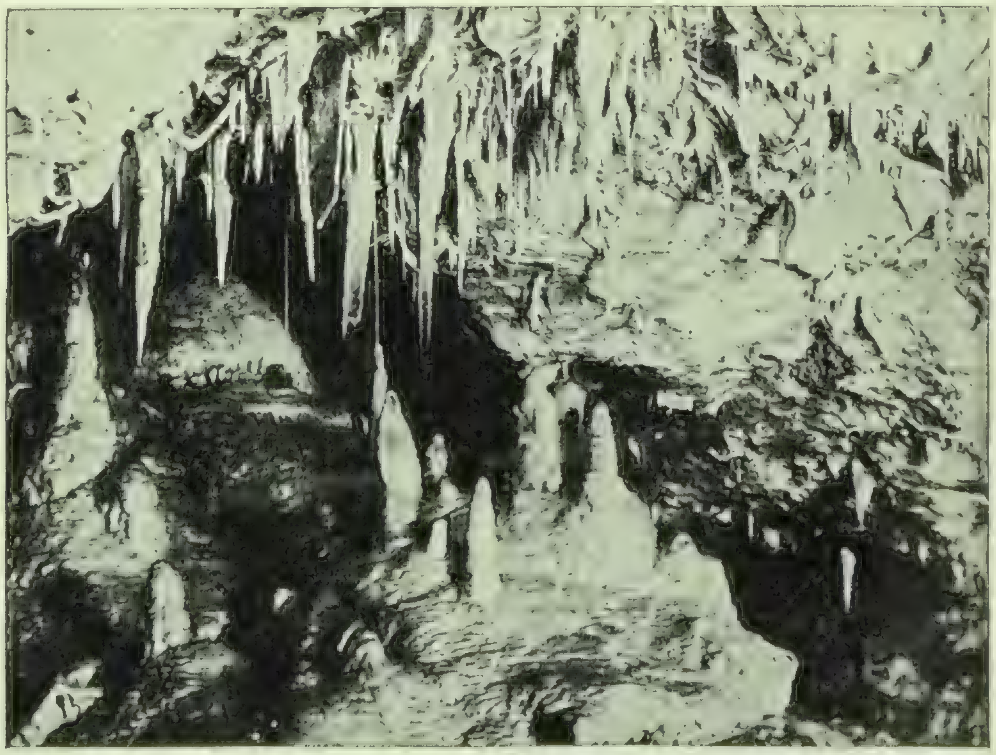
$$Ca(HCO_3)_2 \longrightarrow CaCO_3\downarrow + CO_2\uparrow + H_2O$$

There is a small amount of carbon dioxide in the air, and as water falls from the clouds as rain, it reacts with carbon dioxide to form carbonic acid. Calcium carbonate, in the form of limestone, is present in nearly all soils. Thus, as rain water flows through the earth, the carbonic acid in the water reacts with the normal carbonate ($CaCO_3$) to produce the bicarbonate, $Ca(HCO_3)_2$. Of course, natural waters containing this compound will form an insoluble deposit of calcium carbonate when heated in kettles or boilers.

The carbonic acid, present in rain water, plays an important part in the formation of caves in limestone areas. The water which filters through the limestone rocks at a considerable distance below the surface is under pressure. It will be recalled that water dissolves more of a gas under pressure, and so this underground water in the limestone deposits will contain more carbon dioxide in solution than it could hold at the normal pressure of the air. This fact tends to drive the following reversible reaction to the right.

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2$$

However, when this solution, under pressure, flows through the rocks into a cave, the pressure upon the solution is greatly



Courtesy of the W. Australian Government

FIG. 162—STALACTITES (GROWING DOWN FROM THE ROOF) AND STALAGMITES (GROWING UPWARD FROM THE FLOOR) IN BLACKBOY CAVE, W. AUSTRALIA

decreased, and carbon dioxide is given off as a gas. This will cause the above reversible reaction to go to the left, and so the soluble bicarbonate will be converted into the insoluble carbonate. If the calcium carbonate adheres to the roof of the cave and collects there year after year, where drops of the solution drip through, an icicle of marble, which hangs from the ceiling of the cave will be formed. It is known as a *stalactite.* However, in some cases, this peculiar formation of calcium carbonate is produced by drops of the solution falling at some place on the floor of the cave. It is then known as a *stalagmite.* Sometimes, a stalactite and a stalagmite meet, and then there is a pillar of marble in the cave. Examples of these interesting natural formations are shown in Fig. 162.

3. Uses of Calcium Carbonate

(1) NATURAL CALCIUM CARBONATE. Every year several million tons of limestone are used to make quicklime, and a much larger quantity of limestone is used as a *flux* in the production of pig iron in the blast furnace. Much limestone is needed in the manufacture of *Portland cement.* Of course, marble is used as a *building material* and for *monuments.* Limestone is required in the production of *glass* and *washing soda.* Sometimes limestone is used as a *ballast* in road building.

(2) PRECIPITATED CHALK. Precipitated chalk is the chief component of *tooth powder* and *pastes.* *Whiting* consists of finely ground and carefully cleaned chalk. It is used in polishing powders, pigments, and *putty.* Putty is made by mixing whiting with linseed oil and, sometimes, white lead is added. The addition of the white lead gives a better grade of putty.

CALCIUM OXIDE

1. Preparation

Calcium oxide, commonly known as quicklime, is prepared by heating limestone to about 1000° C. At this temperature the carbonate decomposes into carbon dioxide and calcium oxide, CaO.

$$\underset{\text{(limestone)}}{CaCO_3} \rightleftharpoons \underset{\text{(quicklime)}}{CaO} + CO_2$$

When the above reaction is performed in an open container so that the gas can escape readily, the reaction goes almost completely to the right. This process of converting limestone into quicklime is called lime burning, and the open vessels which are used for this purpose are known as *kilns.*

Lime (CaO) is made in commerce in two types of kilns, the vertical and the rotary. A vertical kiln, as shown in Fig. 163, consists of a steel cylinder lined with firebrick. It is about 75 feet in height and about 10 feet in diameter. The limestone, in the form of lumps, is fed into the kiln at the top, and the quicklime is collected in cars at the bottom. Heat for the process is furnished by fire boxes near the bottom. The boxes open directly into the kiln and supply a draft which sucks in air at the bottom of the apparatus to assist in taking away the carbon dioxide. As a rule, coal is used to supply the heat in the kiln, but wood or gas is sometimes used for this purpose. Rotary kilns, like those used in making cement (see page 488), are used for the conversion of finely powdered calcium carbonate into lime.

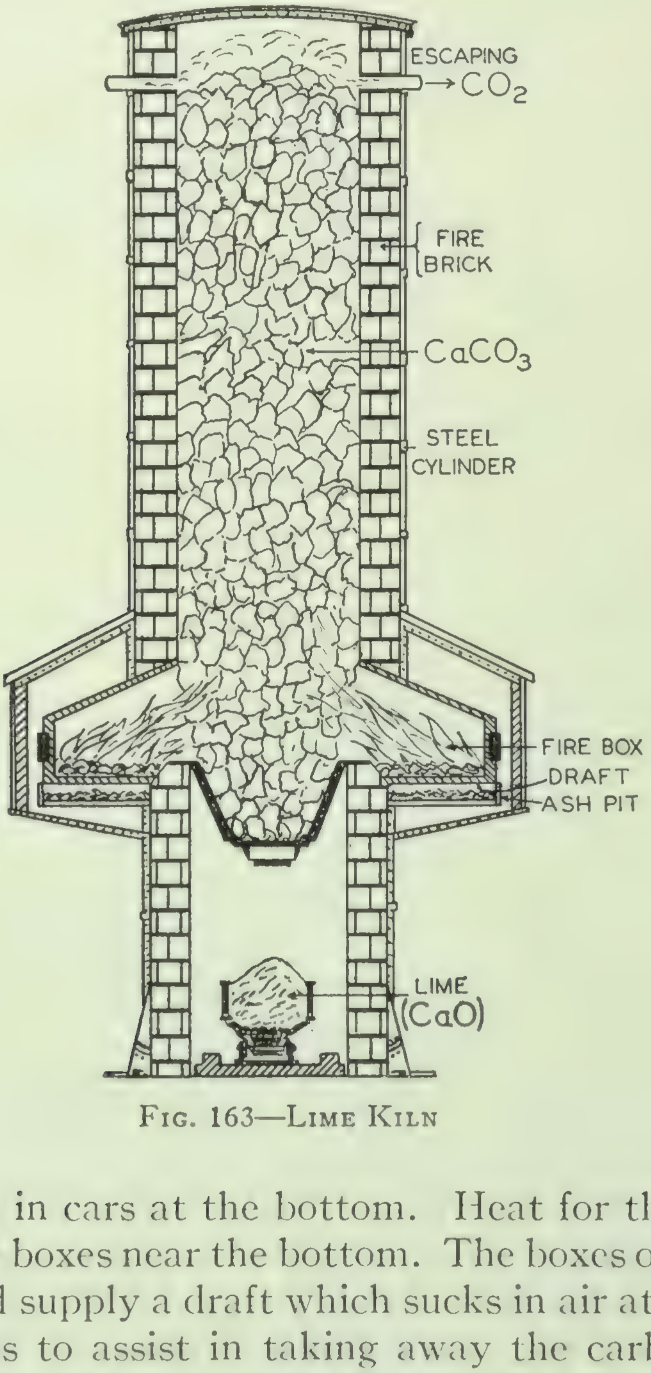


Fig. 163—Lime Kiln

Most of the metal carbonates are, like calcium carbonate, decomposed when heated. For example, lead carbonate forms

$$PbCO_3 \longrightarrow PbO + CO_2\uparrow$$

lead monoxide when it is heated in an open vessel. Copper carbonate also decomposes in a similar manner.

$$CuCO_3 \longrightarrow CuO + CO_2\uparrow$$

2. Properties of Calcium Oxide

(1) PHYSICAL. (a) Pure calcium oxide is a white, amorphous solid. Commercial lime, however, is usually slightly brown or yellow in colour because it contains iron compounds and other materials as impurities.

(b) It can be melted only at a temperature of about 2600° C.

(c) When lime is heated to a high temperature, it gives off a very bright light known as "lime-light."

(2) CHEMICAL. (a) When quicklime is fresh, *it reacts vigorously with water* to produce the base calcium hydroxide. Much heat is liberated in this reaction which is known as the "slaking" of lime. In industry calcium hydroxide is called "slaked lime" or "hydrated lime." It is to be remembered, however, that it is not a hydrate but a base.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

A solution of this base is known as lime-water, and it is used as a reagent to show the presence of carbon dioxide. The clear lime-water turns milky due to the formation of calcium carbonate when CO_2 is bubbled into it.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow + H_2O$$

If, however, more CO_2 is bubbled into this milky suspension, it is observed that the mixture turns clear. This is due to the fact that the excess of carbonic acid produced converts the calcium carbonate into calcium bicarbonate which is soluble in water.

$$CaCO_3 + H_2CO_3 \longrightarrow Ca(HCO_3)_2$$

(b) Calcium oxide reacts with carbon dioxide to form calcium carbonate.

$$CaO + CO_2 \longrightarrow CaCO_3$$

This reaction takes place when quicklime is exposed to air for some time. Water is also absorbed from the air to produce the hydroxide. When these two reactions take place, it is said that the lime is "air-slaked." This product has no commercial value. The following equation would represent the process.

$$2\,CaO + H_2O + CO_2 \longrightarrow Ca(OH)_2 + CaCO_3$$

3. Uses of Calcium Oxide

(1) Lime, mixed with water, is used a great deal in industry as an inexpensive *base*, being considerably cheaper than sodium hydroxide.

(2) Quicklime is used in large amounts in the making of *mortar* and *plaster;* this use will be discussed in some detail in the next section.

(3) Calcium oxide is used in the manufacture of chloride of lime or bleaching powder ($CaOCl_2$).

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$

(4) It is used to remove hair from the hides of animals in the manufacture of leather.

(5) Lime is also used in the manufacture of citric, tartaric and other organic acids.

(6) Quicklime finds important applications in the metallurgy of nickel, lead, copper and other metals.

(7) A new use for lime is its application in the manufacture of a new plastic from pulp-mill waste liquor. This process may result in the production of one of the cheapest of all plastics.

(8) The use of calcium carbonate filler instead of imported clay in newsprint and magazine paper has created a new market for white, high-calcium lime in Canada. At present, paper companies using this type of filler, buy the quicklime and produce the calcium carbonate filler at their own factories.

(9) Lime is required in the making of building brick, pottery, silica brick and sand-lime brick.

(10) It is used in the chemical industry in the manufacture of fertilizers.

(11) Lime is added to acid farm land to sweeten the soil.

MORTAR AND PLASTER

1. Preparation

(1) Mortar. Mortar is prepared by mixing quicklime and sand with a slight excess of water. If much weight is to be carried by the wall and, if the construction of the building must be rapid, then Portland cement is mixed with the mortar.

(2) Plaster. For many years plaster has been prepared by mixing lime, sand, a binding material, such as horse hair, and water in slight excess. A base coat of plaster was then added to wood lathes. When the plaster was nearly dry, an outer coat, consisting of a mixture of lime, plaster of Paris and glue, was applied.

According to modern practice, the base coat of plaster is applied over gypsum lath; wood lath having almost disappeared from use in first class building construction. The base coat plaster is usually a mixture of the following: dehydrated gypsum (plaster of Paris), a small amount of hair, sand, and water. This mixture adheres strongly to the lath, furnishing a rough, grey surface on which the finishing coat is applied. The most common plaster finish consists of lime putty (CaO) and plaster of Paris; it gives a smooth white surface to wall and ceilings.

2. Hardening of Lime Mortar and Lime Plaster

The first stage of the hardening of lime mortar or lime plaster appears to be the drying out of the mechanically mixed water. This is a physical change. The first chemical reaction is probably the combination of water with calcium oxide to form calcium hydroxide.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

The next chemical change to take place appears to be the combination of the carbon dioxide of the air with calcium hydroxide to form calcium carbonate.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

The above reaction is extremely slow and sometimes builders burn coke in fire-baskets in new houses to speed up this reaction.

The sand serves a double purpose in the mixture of lime mortar or lime plaster. It keeps the mass so porous that carbon dioxide can penetrate readily, and it prevents excessive shrinkage on drying and hardening.

CALCIUM SULPHATE

Calcium sulphate is found in nature as *gypsum*, $CaSO_4$ $2\,H_2O$. The anhydrous compound, $CaSO_4$, occurs as the mineral *anhydrite*. Gypsum deposits are located in many parts of the world. Canada is fortunate in possessing large deposits of high grade gypsum. These are located in the Maritime provinces, Ontario, Manitoba and British Columbia. Gypsum has a number of interesting uses. Blackboard crayon (chalk) is made from it. It is also mixed with cement to slow up the rate of setting. Gypsum is used in the production of paper, paints, and certain fertilizers.

Plaster of Paris is formed when gypsum is heated to a temperature of about 170° C. The dihydrate, $CaSO_4.2\ H_2O$, gives up some of its water of crystallization to form a lower hydrate. It is a reversible reaction and it can be represented by the following equation.

$$2\ CaSO_4.2\ H_2O \rightleftharpoons (CaSO_4)_2.H_2O + 3\ H_2O$$

The name, plaster of Paris, originated many years ago when most of it was obtained from Paris. When plaster of Paris is mixed with water, it is changed back into gypsum. Due to the fact that it sets rapidly and expands when it solidifies, plaster of Paris can be used to make surgical casts (for broken bones), models, molds and statuary. It has already been pointed out in the previous part of this chapter that an important use of plaster of Paris is in the production of plaster to cover the inside walls of buildings. *Stucco* is often made by mixing plaster of Paris with glue. Wall board, used extensively in building, is produced by mixing plaster of Paris and wood pulp. In some cases, wall board is manufactured by binding sheets of paper together with layers of plaster of Paris.

HARD WATER

It was discovered in the section on calcium carbonate that calcium bicarbonate, $Ca(HCO_3)_2$, is formed when rain water

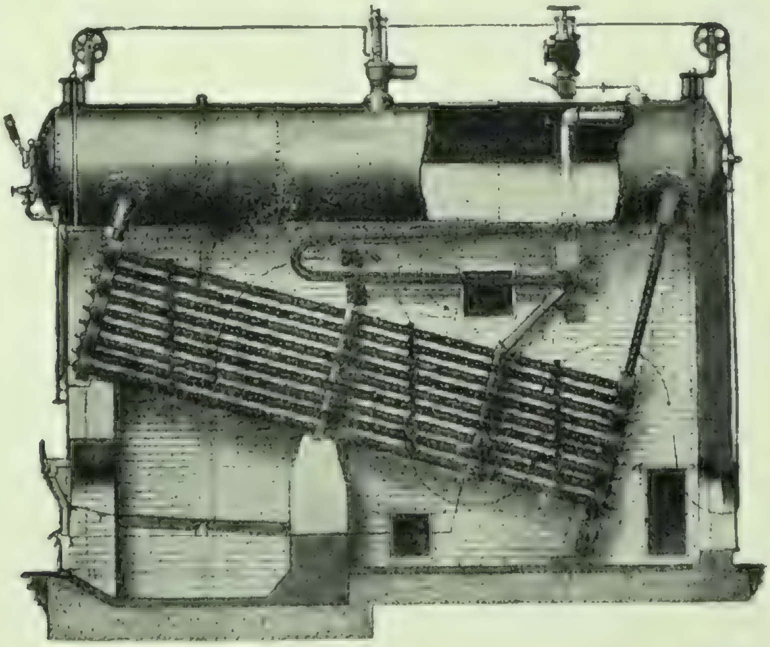


FIG. 164—WATER-TUBE BOILER, FITTED WITH SUPERHEATER

flows through the soil. Magnesium bicarbonate may also be produced in the same way. Water which contains these or other salts of calcium and magnesium in appreciable amounts is known as *hard* water. On the other hand, waters which are almost free of these ions are said to be *soft*. The calcium and magnesium ions are usually present as the bicarbonate, sulphate, and chloride. Waters which contain only calcium and magnesium bicarbonate are said to possess *temporary hardness*, because the calcium and magnesium ions can be readily removed as $CaCO_3$ and $MgCO_3$ by boiling.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + CO_2\uparrow + H_2O$$

However, when calcium and magnesium are present as the sulphate or chloride, they cannot be precipitated out of the solution by boiling. Such waters are said to possess *permanent hardness*, and other methods of softening must be used.

Hard waters are wasteful of soap when used in laundry work, and they produce a deposit in boiler tubes. This deposit is known as "boiler-scale," and its presence may cause a serious explosion. It also increases the cost of heating the water as more heat must be applied to the boiler tubes to get up steam.

There are a number of substances which can be used to soften water. They remove the calcium and magnesium ions in the form of insoluble precipitates. Washing soda, Na_2CO_3, is used a great deal for this purpose. It precipitates the calcium and magnesium ions as the carbonates.

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + Na_2SO_4$$

Other chemicals used for this purpose include the following: ammonium hydroxide, calcium hydroxide, borax ($Na_2B_4O_7$) and sodium phosphate (Na_3PO_4).

Many people use the permutit process for softening water. This process consists of passing the water through a receptacle containing a substance known as permutit, which has the formula $NaAlSiO_4$ (See Fig. 165). This compound reacts with the calcium and magnesium ions in water to form insoluble

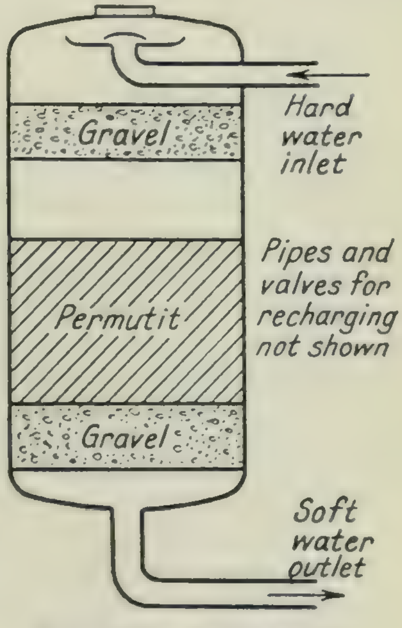


Fig. 165—A Permutit Water Softener

compounds. For example, the reaction with calcium sulphate and permutit is as follows:

$$CaSO_4 + 2\ \underset{\text{(sodium permutit)}}{NaAlSiO_4} \longrightarrow \underset{\text{(calcium permutit)}}{Ca(AlSiO_4)_2} + Na_2SO_4$$

This is a reversible reaction, and so by the addition of a concentrated sodium chloride solution permutit can be obtained again from the calcium permutit.

$$2\ NaCl + Ca(AlSiO_4)_2 \longrightarrow 2\ NaAlSiO_4 + CaCl_2$$

EXERCISES

1. Write a brief note on the occurrence of calcium.
2. Describe the electrolysis of fused calcium chloride. Make a labelled drawing to illustrate your answer.
3. (a) Tabulate three physical properties of calcium.
   (b) Tabulate five chemical properties of calcium.
   (c) Make a list of four uses of calcium.
4. Write a note on the occurrence of calcium carbonate.
5. Tabulate four properties of calcium carbonate.
6. Why do most natural waters contain calcium bicarbonate. Use equations to illustrate your answer.
7. Write a note on stalactites and stalagmites.
8. Tabulate five uses of calcium carbonate.
9. Discuss the commercial production of lime. Make a drawing of a lime kiln.
10. Write equations for the decomposition of the carbonates of calcium, lead, and copper.
11. (a) Tabulate three properties of calcium oxide.
    (b) Tell what takes place when carbon dioxide is bubbled for some time into lime-water. Write equations for the reactions involved.
    (c) What is meant by the air-slaking of lime?
12. Tabulate five important uses of lime.
13. Write a note on mortar and plaster.
14. (a) What is gypsum?
    (b) What is plaster of Paris and how is it prepared?
    (c) Tabulate five uses of plaster of Paris.
15. (a) What is hard water?
    (b) What is meant by the terms temporary and permanent hardness?
    (c) Discuss the problem of water softening and tell how this problem may be solved.

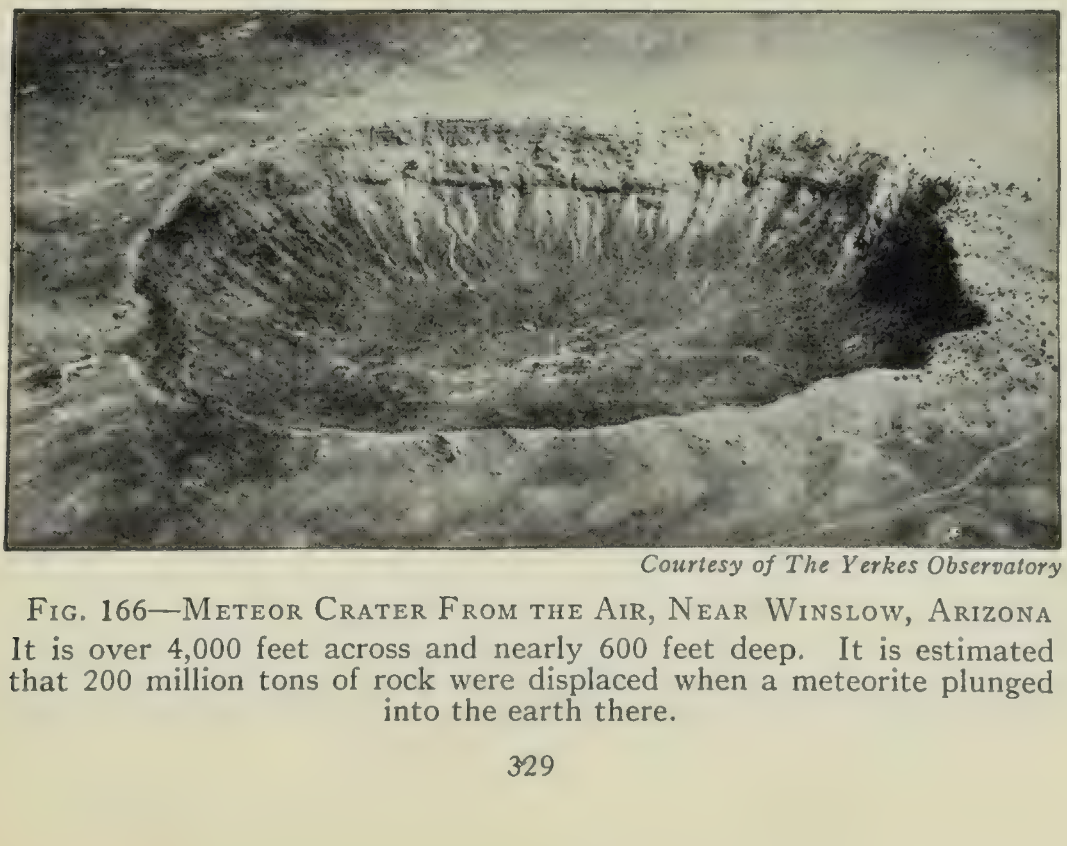
CHAPTER XLII

IRON

1. Importance and Occurrence

Iron is the most important metallic element known. It has played a very important role in the history of mankind. For centuries iron has been the most useful of all the metals, and no other one metal has contributed so much to the welfare and comfort of man. There is scarcely an article used in our daily lives which has not been produced either from iron or by means of it. Furthermore, iron is the cheapest of all the metals, and so most of our modern conveniences are produced from this material. The railroad, the automobile, and the watch are three outstanding examples of such conveniences. Iron is needed to produce our modern tools and machines which provide man with the weapons of war and the implements of peace.

Iron occurs very abundantly in nature and makes up about five per cent of the earth's crust. Scientists have calculated that the centre of the earth consists of a sphere of metallic iron 4,000 miles in diameter; covering this sphere is a layer of silicate of iron and magnesium 1,000 miles thick. If this be



Courtesy of The Yerkes Observatory

FIG. 166—METEOR CRATER FROM THE AIR, NEAR WINSLOW, ARIZONA
It is over 4,000 feet across and nearly 600 feet deep. It is estimated that 200 million tons of rock were displaced when a meteorite plunged into the earth there.

true, then the supply of iron is limitless, provided we can get at it.

Iron is oxidized readily in air containing water and carbon dioxide and, therefore, very little free iron is found in nature. It is found in the free state in most *meteorites;* it may make up the entire mass; or it may occur as very small particles spread throughout some stony material.

Iron is found combined with other elements in many minerals and in most rocks and soils. It is a constituent of the *green colouring matter of plants* and the *haemoglobin* of the blood of animals, and so it plays a very important part in life processes.

Most of our commercial iron is produced from four ores. They are the oxides known as *hematite* (Fe_2O_3), *limonite* ($2Fe_2O_3 . 3H_2O$), *magnetite* (Fe_3O_4), and a carbonate called *siderite* ($FeCO_3$). The sulphide, known as *iron pyrites* (FeS_2), occurs quite widespread in nature, but it is not used as a source of iron.

It is interesting to know that a rich ore contains more than 50 per cent of iron. An average ore has from 35 to 50 per cent of iron, and a low grade ore, which is only worked under favourable conditions, from 25 to 35 per cent. Ores with an iron content of less than 25 per cent of iron are at present considered of no commercial value.

Hematite, known by the chemist as ferric oxide (Fe_2O_3), is the most important of all iron ores. This ore is found in large quantities in the neighbourhood of Lake Superior in the states of Minnesota, Wisconsin and Michigan. The Mesabi range in Minnesota yields more ore than any other in the world. It produces about four-fifths of the entire output in the United States. This deposit is nearly 100 miles long, extending in an easterly and westerly direction about 50 miles northwest of Duluth, Minnesota.

The ore of the Lake Superior district lies near the surface of the ground. It can be mined cheaply with steam shovels. This is known as the open-pit method of mining. Giant ore boats, capable of transporting 12,000 tons of ore, carry the hematite to ports along the lower Great Lakes. Modern methods of loading and unloading have been developed, so that 12,000 tons of ore can be loaded into a vessel inside of 20 minutes. It requires about 4 hours to unload this large quantity of ore.

Canada has never produced a great deal of iron ore, although some has been mined from time to time since the days of the

French regime. In 1899, a deposit of hematite, that later developed into the Helen mine, was located in the Michipicoten area north of Lake Superior in Ontario. This mine was the chief source of supply for years. However, in 1918 this deposit was exhausted and Canadian blast furnaces secured their ore almost entirely from the United States and Newfoundland. In 1938 a large deposit of hematite was discovered at Rock Lake, west of Port Arthur. This deposit was found to be of a quality equal to or better than that of the Minnesota ore, containing about 56 per cent of iron. However, this rich deposit was covered by more than 120,000 million gallons of water, varying in depth from 50 to 265 feet. Engineers have been successful in removing the water from Steep Rock Lake, and recently open-pit mining of the ore has commenced.

Rich deposits of hematite have recently been discovered in Labrador. The most important deposit appears to be at Sawyer Lake, which is 284 miles north of Seven Islands, Quebec. Analysis of surface samples of this ore shows that it contains about 65 per cent iron. The data already obtained indicates that this is one of the important hematite deposits of the world and it will likely be developed soon.

Hematite gives a red colour to certain soils and rocks, and finely powdered hematite is used a great deal in commerce as a pigment. Limonite, sometimes known as brown hematite, gives a brown colour to certain soils. It is present in many ordinary clays; and when they are used to make brick and earthenware, the material turns red on being heated to a high temperature. Magnetite, as its name suggests, is attracted by a magnet. This fact is sometimes used in separating this mineral from crushed earthy material. Lodestone, a natural magnet, is a variety of magnetite.

2. The Blast Furnace

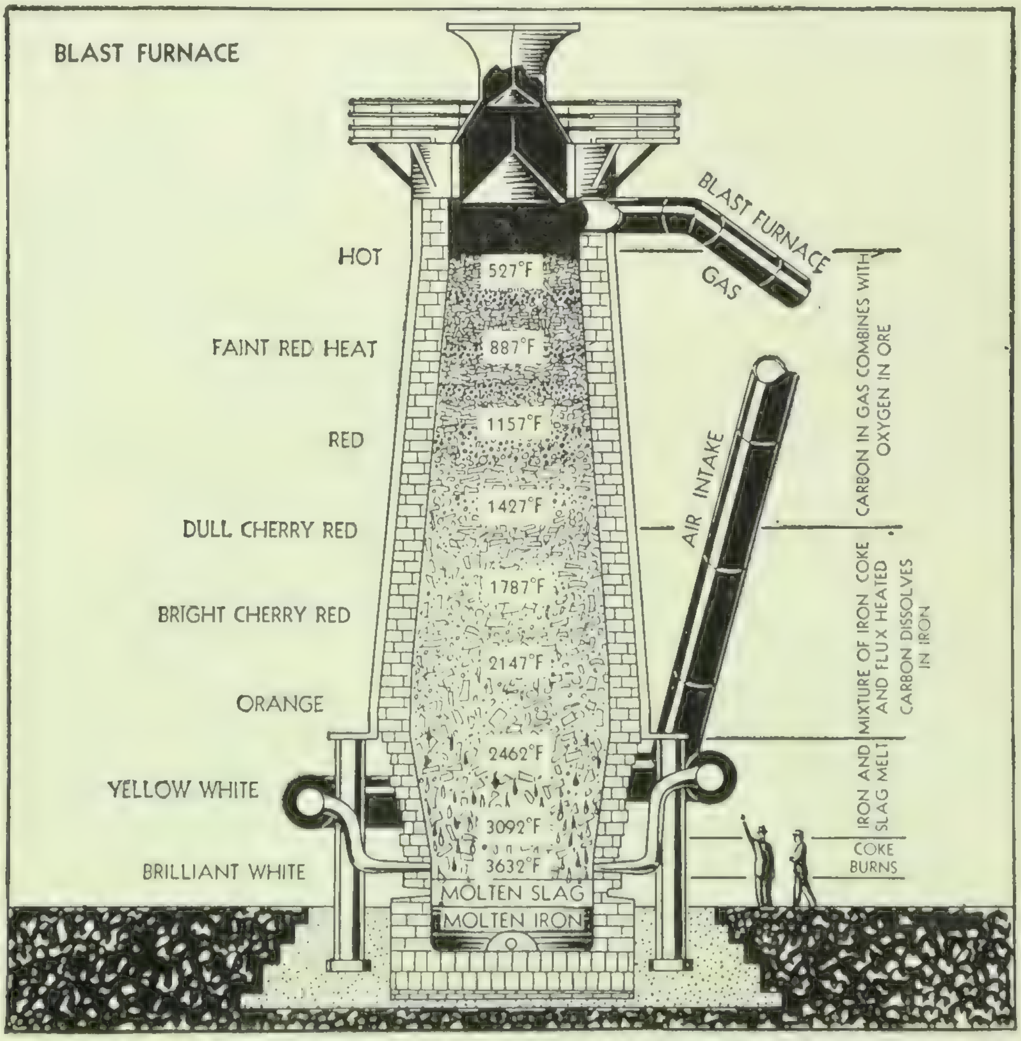
It has already been pointed out that the chief ore in America is hematite (Fe_2O_3). In addition to the oxide, the ore contains a large proportion of worthless material known as *gangue*. The gangue is a mixture consisting chiefly of the following: quartz, limestone, sand and silicates. The first step in the conversion of iron ore to iron and steel takes place in the blast furnace. The blast furnace brings about three important things:

(1) It separates the gangue from the ore.

(2) It releases the iron from the oxygen with which it is combined. This is accomplished by the chemical reduction of the oxide with carbon in the form of coke and carbon monoxide, formed when carbon dioxide passes over the hot coke.

(3) It adds the carbon which the soft iron must have to give it stiffness.

The process which takes place in the blast furnace is known as *smelting.*



Courtesy of General Motors Products of Canada, Ltd.

FIG. 167—THE CROSS-SECTION OF AN IRON BLAST FURNACE

The blast furnace is a huge shell or tower, sometimes more than 100 feet in height. It is lined with a special type of brick, called fire-brick, which can withstand very high temperatures. The furnace widens from the bottom to a diameter of about 22 feet and then tapers again toward the top. It is called a blast furnace because a powerful blast of air is produced by blowing dry, heated air, under great pressure, into the furnace through pipes near the bottom. These pipes are known as *tuyères*.

The process is continuous and a blast furnace once started is kept in operation until repairs are required. Some furnaces have been in operation continuously for several years. The materials which are fed into the top of a blast furnace are known as the *charge* and it consists of:

(1) The iron ore, made up of ferric oxide (Fe_2O_3) and gangue;
(2) The flux, usually limestone;
(3) The fuel, coke.

A mixture of these materials, in the proportions of two tons of ore to one ton of coke and one-quarter of a ton of limestone, is fed into the top of the furnace by huge buckets operating on an inclined track. The buckets keep the furnace filled with successive layers of iron ore, limestone, and coke.

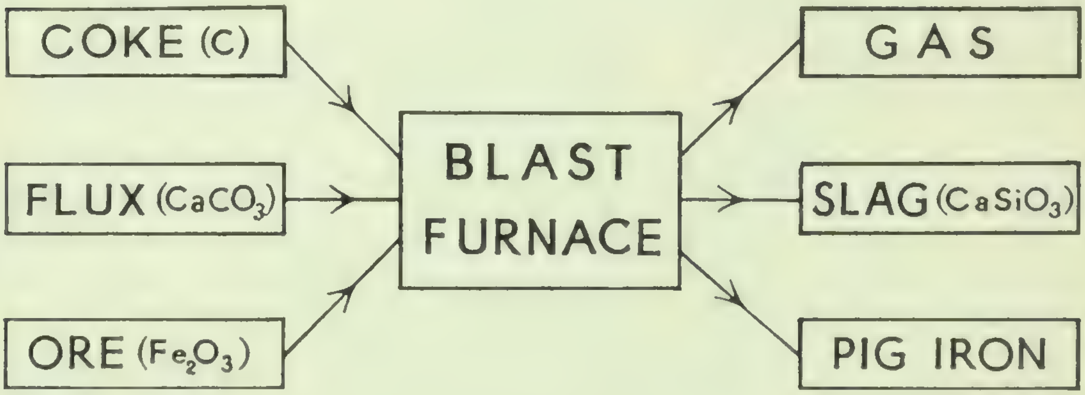
The blazing gas fire of the furnace, made still hotter by the blasts of hot air entering through the tuyères, reduces the ore to a liquid state. The flux combines with the gangue in the ore to produce a fusible (molten) product which is known as the *slag*. If the gangue is chiefly silica (SiO_2), then the flux must be limestone. However, if the gangue consists of lime or magnesia, then the flux must be silica. Since most of the iron ores on this continent contain silica as the gangue, limestone is the chief flux used in the blast furnace. The oxygen of the air comes in contact with the red hot coke and the fuel burns to produce carbon dioxide. This compound is reduced at once to carbon monoxide. The reduction of ferric oxide to metallic iron is brought about partly by the carbon monoxide and partly by the coke.

The temperature of the furnace, as shown in Fig. 167, is greatest near the tuyères, where the greatest amount of combustion takes place, and decreases as the distance upwards increases. The reduced iron trickles down over the hot coke, absorbs carbon, and drops to the hearth, or bottom of the furnace. The slag, being lighter in weight than the molten iron, floats on the surface of the metal.

The gases, which escape from the top of the furnace, are known as "*blast furnace gases*." They consist of a mixture of about 25 per cent carbon monoxide, 60 per cent nitrogen, and the remaining 15 per cent is a mixture of carbon dioxide, hydrogen and hydrocarbons. These gases are cleaned and used either to operate gas engines around the furnace, or as a fuel to heat the so-called *hot blast stoves*, which are used to heat the air blown into the blast furnace through the tuyères.

About every four hours, the molten iron and slag are tapped out of the hearth into separate ladles. This operation is known as "tapping" and the molten iron, ranging from 80 to 120 tons, is called a "heat." This flows out in a fiery, hissing stream into huge ladles, which can be quickly transported to a steel furnace, if the iron is going to be made into steel, or it is cast into "pigs."

The average daily production of an ordinary blast furnace is about 600 tons of iron. However, some of the largest furnaces produce about a 1000 tons per day. Such a furnace would need about 2000 tons of hematite ore, almost 1000 tons of coke, 500 tons of limestone and nearly 5000 tons of air. A summary of the materials used and the products obtained in a blast furnace is given below:



3. Chemical Reactions in the Blast Furnace

$$\underset{\text{(flux)}}{CaCO_3} + \text{heat} \longrightarrow CaO + CO_2\uparrow$$

$$CaO + \underset{\substack{\text{silicon dioxide}\\\text{(gangue)}}}{SiO_2} \longrightarrow \underset{\substack{\text{calcium silicate}\\\text{(slag)}}}{CaSiO_3}$$

At the bottom of the furnace the following reactions take place:

$$C + O_2 \longrightarrow CO_2 + \text{heat}$$

$$CO_2 + C \longrightarrow 2\ CO$$

$$Fe_2O_3 + 3\ CO \longrightarrow 2\ Fe + 3\ CO_2$$

4. Pig Iron

When the blast furnaces were first operated many years ago, the molten iron was drawn off directly into sand moulds or troughs. These seemed to look like a litter of little pigs lying along side their mother and feeding. This is how the name "pig iron" came to be used for the product of the blast furnace.

Today the liquid iron is either taken quickly to the steel mill for immediate conversion into steel, or transported to the "pig" casting machine which has replaced the old sand moulds. "Pigs" are easy to store or to transport. Until recently the "pigs" varied in weight from 60 to 200 pounds. Recently, however, their weight has been reduced considerably, and they now vary in weight from 45 to 60 pounds. There are two chief reasons for this reduction in weight. In the first place, they are lighter to lift and so easier to handle. Secondly, the smaller pieces of iron are easier to melt, and so less fuel is required for bringing about the change to the liquid state.

The product of the blast furnace is always called "pig iron" whether or not it ever becomes a "pig." Pig iron is the starting material for nearly every type of iron, such as cast iron, wrought iron, or steel.

Analysis of pig iron shows that it contains certain impurities, such as carbon, manganese, sulphur, phosphorus, and silicon. These impurities make the iron weak and brittle; hence it must be refined before it can be used for many commercial purposes. The analysis of pig iron varies a great deal, depending on conditions in the furnace and the raw materials used. The following is a typical analysis:

	Per Cent
Carbon	3.50
Manganese	2.00
Sulphur	.04
Phosphorus	.30
Silicon	1.25
Iron	92.91

5. Cast Iron

Cast iron is made by melting pig iron and allowing it to cool. There are two kinds of cast iron. If the cooling is a rapid process, *cementite*, an iron carbide, Fe_3C, is produced. This compound is present in the iron in a solid solution which is known as *white cast iron.* This material is very hard and brittle. On the other hand, if the cooling process is slower, a high percentage of the carbon separates out from the iron in the form of graphite, and the product is known as *gray cast iron.* This substance is much softer than white cast iron.

Cast iron has a relatively low melting point (1150°-1250° C.). When molten cast iron changes to the solid state it expands and completely fills the mould into which it was poured. Thus, it is an excellent material for casting. Of course, it cannot be welded, rolled, or forged; it possesses a low tensile strength. Cast iron is readily broken and therefore cannot be used to produce articles which will be subjected to violent shock or strain. It is very well suited for many other uses such as the manufacture of stoves, steam radiators and certain kinds of machinery.

White cast iron may be changed to a malleable substance by heating it at a red heat for two or three days and then cooling it very slowly. As a result of this treatment, most of the carbon in this substance separates out as small particles of graphite. The product is known as *malleable cast iron* which is stronger than cast iron. Also it can stand more shock and is cheaper than steel. Malleable cast iron is used for the manufacture of certain parts of locomotives, automobiles and other machines.

6. Wrought Iron

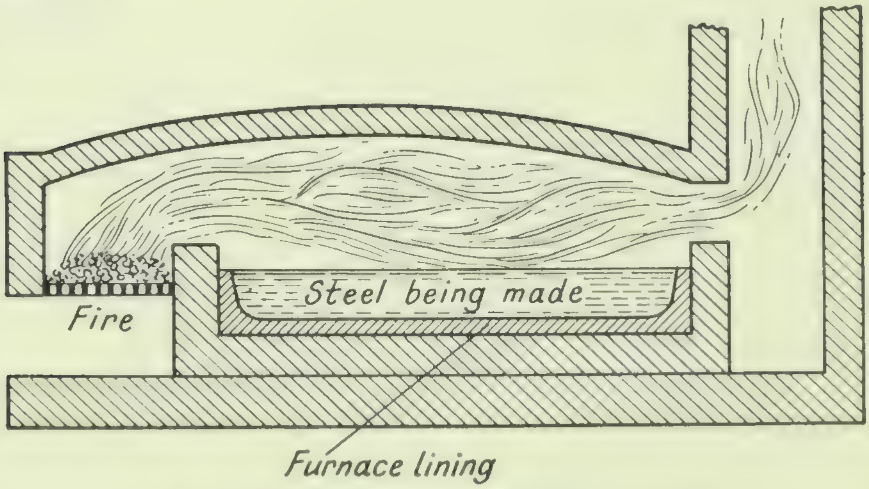


FIG. 168—A REVERBERATORY FURNACE

Wrought iron is a tough, malleable type of iron product which contains not more than 0.2 per cent of carbon. It is made by heating *pig iron* in a reverberatory furnace which holds about 1500 pounds of the final product. A reverberatory furnace is one in which the heat produced by the coal fire is reflected down on to the hearth by the sloping sides and roof, as shown in Fig. 168. The hearth of the furnace is covered with hematite, Fe_2O_3, and then the charge of pig iron is added. The metal soon changes to the liquid state, the carbon of the pig iron being removed chiefly by the oxygen of the ferric oxide according to the following equation.

$$Fe_2O_3 + 3\,C \longrightarrow 2\,Fe + 3\,CO\uparrow$$

The escaping carbon monoxide burns and this increases the temperature of the furnace.

$$2\ CO + O_2 \longrightarrow 2\ CO_2 + \text{heat}$$

The sulphur in the pig iron is oxidized to sulphur dioxide, which escapes as a gas. The silicon, manganese and phosphorus are changed into such compounds as iron silicate, manganese silicate and ferric phosphate. These compounds make up a very fusible slag. As the carbon is removed, the melting point of the iron goes up, and so the material in the furnace becomes pasty and thick. A workman, known as the "puddler," continually stirs the charge with a heavy iron rod. When the puddler thinks that the process is finished, he collects the material in lumps or balls weighing about 100 pounds each. The balls are removed and placed between rollers to squeeze out most of the fusible slag.

The chief properties of wrought iron are as follows:
(1) It has a fibrous structure, being built up of layers of pure iron which are separated by thin films of slag.
(2) It is malleable and ductile.
(3) It is softer and stronger than cast iron. However, it is not as strong as steel.
(4) It possesses a high melting point (1500° C.).

Wrought iron is used to produce articles which can be shaped by a hammer while red hot. Anchors, chains, bolts, wire, plowshares and horseshoes are some examples of useful articles made from this type of iron. During recent years wrought iron has been replaced to a certain extent by steels which contain very small quantities of carbon.

7. The Effect of Carbon on the Properties of Iron

Carbon has a marked effect on the properties of iron. For example, pure iron is relatively soft, but pig iron, containing from 2.5 to 4.0 per cent carbon, is a hard metal. Pure iron is malleable, but pig iron does not possess this property. Again, wrought iron, with a carbon content of less than 0.20 per cent, is not brittle, but pig iron is quite brittle. Pure iron melts at 1530° C., but as the carbon content increases, the melting point decreases. Pig iron, however, with a relatively high carbon content melts at about 1100° C. Of course, the properties of a metal regulate its industrial uses. Thus, wrought iron is suitable for making anchors, chains, bolts, and electro-magnets. Pig iron, however, is not suitable for the manufacture of such articles. It can, however, be used to make iron pipes, stoves, radiators and other heavy metallic objects. Table 20 attempts to show the effect of carbon on the properties of iron.

TABLE 20—THE EFFECT OF CARBON ON THE PROPERTIES OF IRON

Type of Iron	Per cent Carbon	Melting Point	Chief Physical Properties	Uses
Pure Iron	0.00	1530°C.	Soft, malleable, not brittle, ductile.	Chemical reagent.
Wrought Iron	Less than 0.15	1500°C.	Soft, malleable, not brittle, readily welded, readily rolled, and forged.	anchors, chains, bolts, electro-magnets, wire-fencing, and grate bars.
Steel	0.08 to 1.50		hardness varies with per cent of carbon, malleable, not brittle, welded.	rails, bridges, machinery.
Pig Iron	2.5 to 4.0	1100°C.	hard, not malleable, brittle, cannot be welded, cannot be rolled or forged.	iron pipes, stoves, heavy metallic objects.

8. Properties of Pure Iron

The chief properties of the metal are:

(1) It has a silvery lustre.
(2) Iron is malleable, ductile, and relatively soft.
(3) It is readily magnetized.
(4) Pure iron melts at 1530° C.
(5) Since it is well above hydrogen in the electromotive series, dilute acids react readily with it to produce hydrogen.

$$\mathbf{Fe + 2\,HCl \longrightarrow \underset{\text{(ferrous chloride)}}{FeCl_2} + H_2\uparrow}$$

(6) Pure iron does not oxidize to form rust in *dry* air. However, it does change to rust slowly in pure water, and in an atmosphere which contains water and carbon dioxide, the oxidation occurs quickly.

$$\mathbf{4\,Fe + 3\,O_2 \longrightarrow 2\,\underset{\text{ferric oxide (rust)}}{Fe_2O_3}}$$

At high temperatures iron combines vigorously with oxygen to form an oxide, known as magnetic iron oxide or hammer-scale.

$$3\ Fe + 2\ O_2 \longrightarrow \underset{\substack{\text{magnetic iron oxide} \\ \text{(hammer-scale)}}}{Fe_3O_4}$$

(7) Hot iron reacts with steam according to the following equation:

$$3\ Fe + 4\ H_2O \rightleftharpoons Fe_3O_4 + 4\ H_2\uparrow$$

(8) Iron is an element which forms two series of compounds, known as ferrous and ferric. In ferrous compounds iron has a valence of two; in ferric compounds it has a valence of three.

9. Some Important Compounds of Iron

Iron forms a number of important compounds and the names, formulas, and chief uses of a few of these are given below in Table 21.

TABLE 21

NAMES, FORMULAS AND USES OF SOME IMPORTANT IRON COMPOUNDS

Name	Formula	Uses
Ferric oxide	Fe_2O_3	Jeweler's *rouge*; *venetian red*, which is used as a pigment in paints for barns, bridges, railway cars, and as a pigment for pottery and rubber.
Green Vitriol (hydrated ferrous sulphate)	$FeSO_4 . 7\ H_2O$	In purification of water; in medicine; as a weed killer and wood preservative; in the manufacture of black inks and dyes.
Ferric chloride	$FeCl_3$	Mordant in the dye industry; in medicine.
Prussian Blue (ferric ferro-cyanide)	$Fe_4(Fe(CN)_6)_3$	As a pigment in paints; bluing for laundries.
Potassium thiocyanate	KSCN	Used as a chemical test for the ferric ion (Fe^{+++}), giving a blood-red colour when added to such ions.

EXERCISES

1. Write a note on the importance and occurrence of iron.
2. Define each of the following terms: gangue, smelting, blast furnace, tuyères, flux, slag.

3. Describe a blast furnace using a labelled diagram to illustrate your answer.
4. Write equations for the chief reactions taking place in the blast furnace.
5. (a) What is cast iron?
   (b) Name the three types of cast iron.
   (c) Explain the difference between these three kinds of cast iron.
   (d) Give three uses of cast iron.
6. (a) What is wrought iron?
   (b) Describe the production of this type of iron and illustrate your answer with a labelled diagram.
   (c) Tabulate five uses of wrought iron.
7. Discuss the effect of carbon on the properties of iron.
8. What kind of iron would be used in the manufacture of each of the following: steam radiators, pen points, anchors, supports for classroom seats and desks, chains, and armour plate.
9. Tabulate five properties of pure iron.
10. (a) What is the difference between ferrous and ferric compounds?
    (b) Name and give one use of the compounds represented by each of the following formulas:
    Fe_2O_3, $FeSO_4 . 7H_2O$, $FeCl_3$.

CHAPTER XLIII

STEEL

Steel may be considered to be iron which has been treated by one or more of several processes. The products formed in this way are known as steels, and they contain from less than 0.1 to more than 1.5 per cent of carbon.

The chief methods of producing steel are:

(1) The Bessemer Process.
(2) The Open Hearth Process.
(3) The Electric Furnace Process.

THE BESSEMER PROCESS

In 1855 Sir Henry Bessemer patented in Great Britain a method of producing steel rapidly in large quantities from pig iron. The product of this process is known as Bessemer steel. This process of making steel was introduced into the United States in 1865.

A large pear-shaped vessel, known as a Bessemer converter, is used in the process. A diagram of one is shown in Fig. 169. The converter is made of steel plates and lined with fire-brick. It is mounted in such a way that it can be rotated for pouring. Air under great pressure is forced into the molten charge of pig iron through numerous small openings in the bottom of the converter.

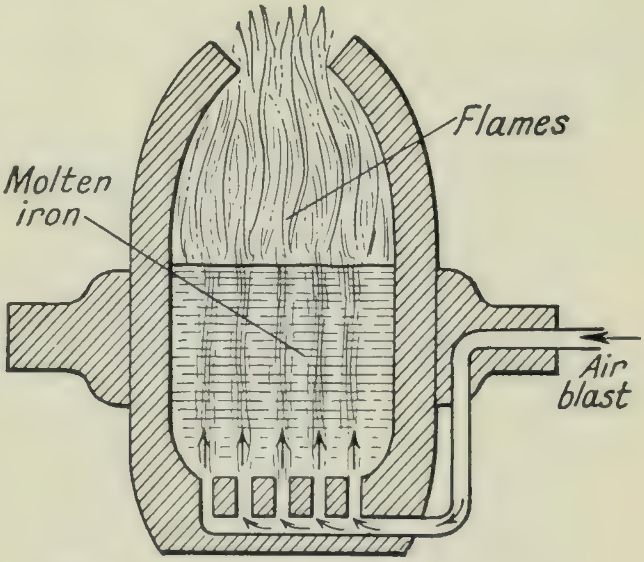


FIG. 169—A BESSEMER CONVERTER

The blast of air burns out or oxidizes the excess carbon and other undesirable components of the pig iron. They leave the converter in the form of gas in a burst of flames and a shower of sparks. The solid impurities, such as the oxides of manganese and silicon, rise to the surface of the metal as slag.

The entire process only takes from 10 to 15 minutes. The men who operate the converter can tell from the colour of the flames when the process has been completed. Because of the heat produced by the oxidation of the carbon and the silicon, the metal is hotter at the end of the "blow" than at the beginning.

The Bessemer process furnishes steel which is suitable for rails and other construction projects. Steel produced by the Bessemer process is much cheaper than that obtained by the Open Hearth process. However, the latter method gives us a better quality steel. Due to this fact, and also because ores suitable for use in the Bessemer process are becoming scarce, about three times as much steel in America is made by the Open Hearth process as by the Bessemer.

THE OPEN HEARTH PROCESS

This process depends upon Sir Wm. Siemens' method of obtaining very high temperatures by the regenerative system. By this means a bath of iron may be kept in a liquid condition at any degree of purity. The Open Hearth process really consists of remelting old steel scrap with varying amounts of pig iron. After the charge is melted, the impurities are oxidized by the addition of ferric oxide (Fe_2O_3), usually as hematite ore or mill scale.

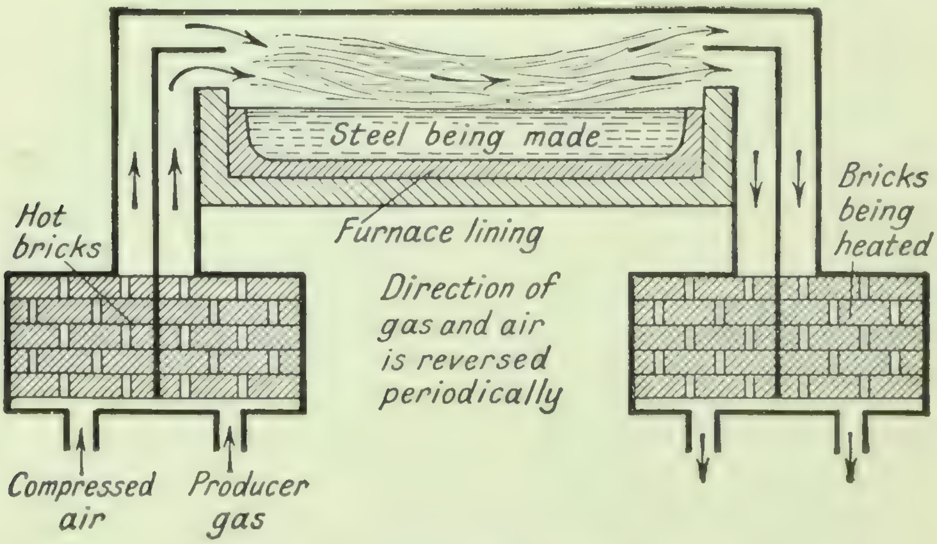


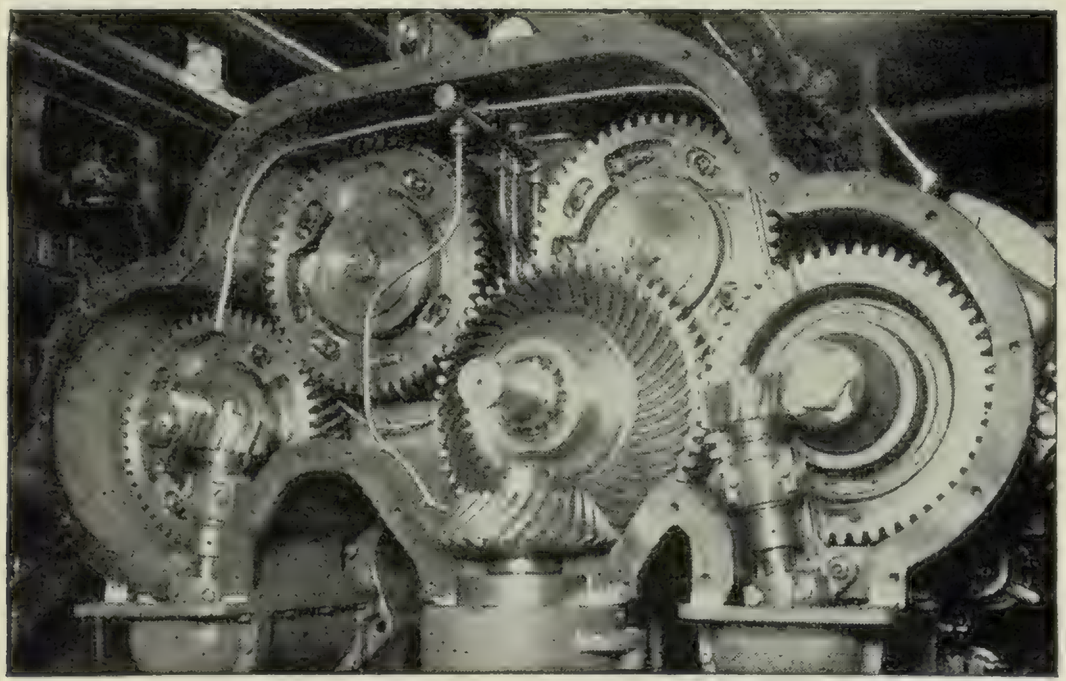
FIG. 170—AN OPEN HEARTH FURNACE

An open hearth furnace is somewhat like a huge oven. A diagram of one is shown in Fig. 170. Usually, several furnaces are built together in a row. They are made of steel and refractory brick, which can withstand very high temperatures.

In the average 75-ton furnace, the hearth is 35 feet long, 13 feet wide, and 2 feet deep.

The hearth is actually a basin in which the purification of the molten iron takes place. It is subjected to very great heat but it is protected from the direct flames of the furnace. The intense heat needed by this process is secured by a device known as the "regenerative furnace." For about 30 minutes fuel gas is admitted through the "ports" or valves on one side, and burns in the furnace. The hot gases, produced by the oxidation of the fuel gas, escape by means of the "ports" on the opposite side. Then the valves are reversed, and the fuel gas and air enter through the hot chambers on that side. This continual reversal at the end of 30 minute periods produces an ever increasing rise in temperature until the charge is ready to be removed. It requires about 12 hours to produce a 75-ton "heat."

This method of producing steel, called the *basic* Open Hearth process, is used by most of the steel plants in Canada and the United States. The furnace linings and the flux material consist of substances which have basic properties, such as magnesite ($MgCO_3$) or dolomite ($MgCO_3 . CaCO_3$). The *acid* Open Hearth process, on the other hand, uses materials for furnace lining and flux which have acidic properties. This method is used to a considerable extent in England, where a large amount of acid



Courtesy of R. Hoe & Co., Inc.

FIG. 171—THESE REMARKABLE HIGH-GRADE STEEL GEARS ARE ON A MODERN NEWS PRESS

Some of the latest types of high speed presses can produce 120,000 16-page newspapers per hour.

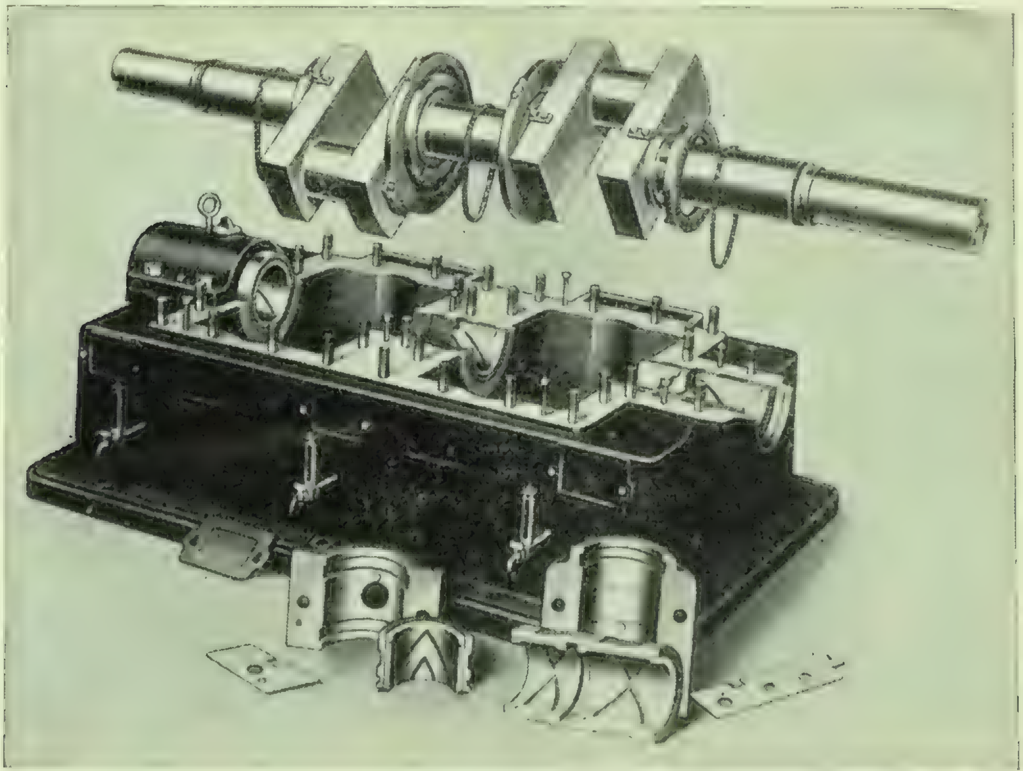
open-hearth steel is needed for the construction of bridges, ships, and other structural purposes. The nature of the iron ore used and the type of steel required regulate which of the two types of Open Hearth process should be used.

THE ELECTRIC FURNACE PROCESS

The electric furnace is used to a very considerable extent in the production of special steels. A tremendous electric arc is struck between carbon electrodes and the charge of liquid iron. The heat produced from the electric arc keeps the furnace hot. A very careful control of conditions is possible in this type of furnace; making possible the production of high-grade steels, which are used in making tools, springs, razor blades, knives, etc.

TEMPERING OF STEEL

All steels which have a carbon content between 0.5 per cent and 1.5 per cent can be *tempered.* At high temperatures all steel contains a compound of iron and carbon, known as cementite, Fe_3C. This compound (a carbide), under such a condition, is soluble in the iron. Upon cooling steel slowly, some of the

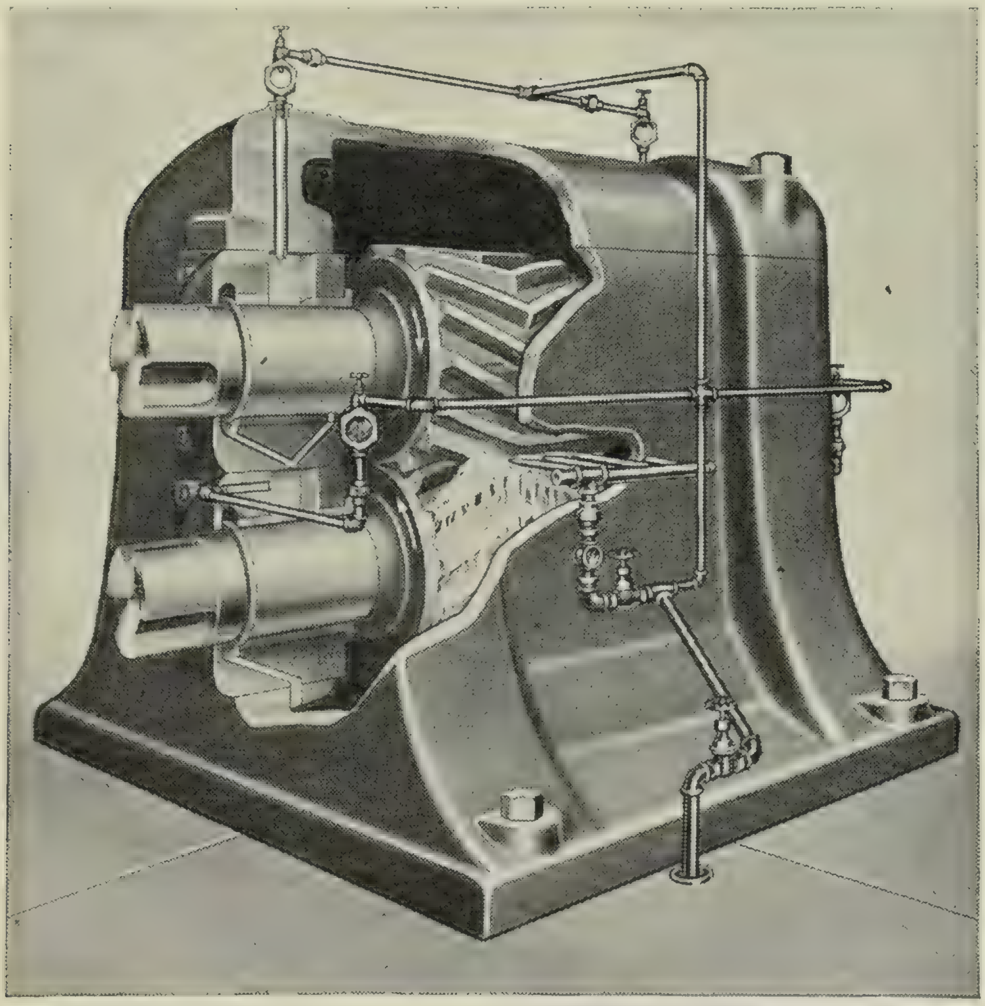


Courtesy of Anderson Diesel Engine Co.

FIG. 172—AN ENGINE BASE, CRANKSHAFT, AND BEARINGS
Alloy steels are needed in the production of the essential parts of motors.

carbide gradually comes out of solution in a crystalline form, and so steel which has been cooled slowly is a mixture of iron and crystals of cementite (Fe_3C). This type of steel is soft and very similar to wrought iron.

On the other hand, if steel at a high temperature, about 700° C. or higher, is chilled quickly, it becomes hard. This is due to the fact that the iron carbide does not have enough time to come out of solution as crystals, and so it stays in solution. Steel chilled suddenly by *quenching* (placing in cold water or oil) has the greatest degree of hardness for the particular steel under consideration. Such a steel is usually too hard for many uses, and so its degree of hardness is changed somewhat (tempered) by slowly *reheating* the cooled steel to temperatures between 200° and 325° C. When cooled quickly a separation of some of the cementite from the iron occurs, and as a result the steel becomes softer and less brittle. This process is known as *tempering*.



Courtesy of S. F. Bowser & Co., Inc.

FIG. 173—A CUTAWAY VIEW OF A SET OF GREAT STEEL MILL GEARS

TABLE 22—ALLOY STEELS

Name	Composition (Percentage)	Chief Properties	Uses
Stainless (Chrome)	14-20 Cr. 8-20 Ni.	Hard, strong, tough and resists corrosion.	Pumps, valves, chemical ware, periscopes of submarines, steam turbines, oil stills, machinery for paper industry, cutlery.
Manganese	10-14 Mn.	Hard, tough and strong.	Steam shovels, safes, grinding machines, jaws of rock crushers.
Silicon (Duriron)	12-14 Si.	Resists corrosion of acids.	Retorts for distilling acids, containers for acids
Nickel	3-4 Ni.	Resists corrosion, strong and tough.	Structural purposes, gun forgings, machine parts, engine and automobile parts.
Chrome-Nickel	0.5-1.75 Cr. 1.0-3.25 Ni.	Hard, great strength, high elasticity.	Automobile shafts and gears, case-hardening, armour plate.
Tungsten	10-20 W. 2- 8 Cr.	Keeps its hardness when red-hot.	High-speed cutting tools.
Permalloy	78.5 Ni.	Remarkable magnetic permeability.	Used in communication industry, especially in the construction of ocean cables, the rate of communication having been increased from 300 to 1,500 signals per minute.
Invar	38 Ni.	Low coefficient of expansion.	Watches, length standards, measuring tapes, sealing in wires in electric light bulbs, etc.
Nomag	10-15 Ni. 5-10 Mn.	Practically non-magnetic.	Motor construction, electrical measuring instruments.

Alloy Steels

Research chemists have found that many useful alloys can be obtained by mixing other metals with steel. These mixtures, known as alloy steels, have made possible certain mechanical devices which man otherwise would have been unable to enjoy. For example, the automobile could not be the useful means of transportation that it is, if it had not been possible to secure alloy steels. Table 22 gives some information concerning a few of the more important steel alloys.

EXERCISES

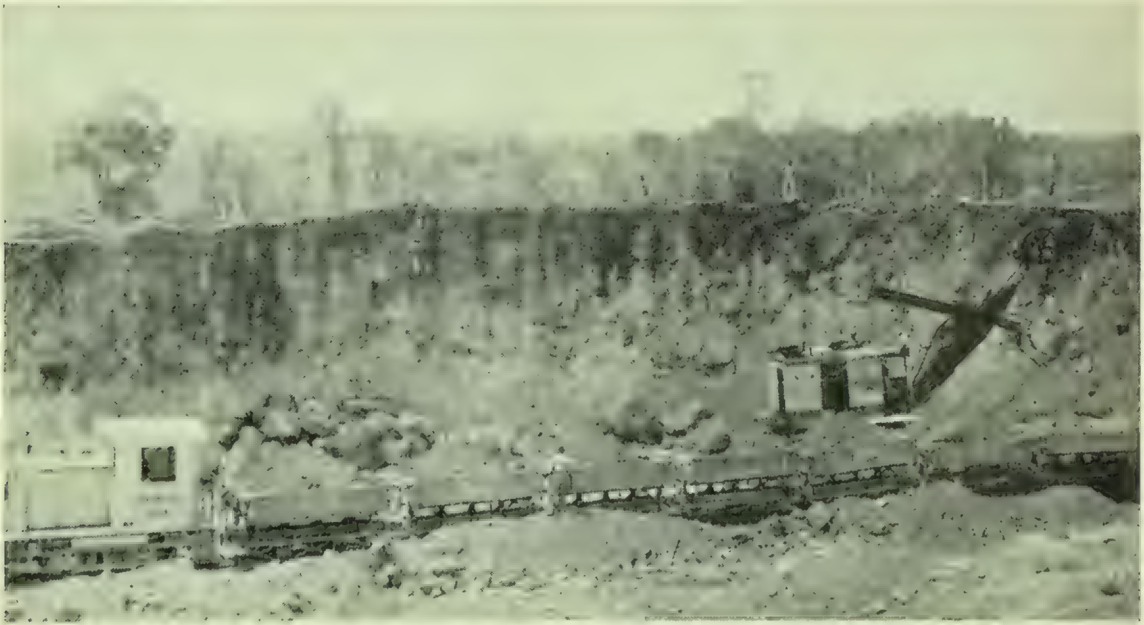
1. (a) What is steel?
   (b) Name the methods of producing it.
2. Write a short note on the Bessemer process.
3. (a) What is the advantage of the Open Hearth process as compared to the Bessemer process?
   (b) What is the essential process in the Open Hearth method?
   (c) Give a brief description of the Open Hearth furnace.
   (d) A device, known as the regenerative furnace, is used in the Open Hearth process. Describe this device briefly.
4. What is the difference between the basic Open Hearth process and the acid Open Hearth process?
5. Write a brief note on the Electric Furnace process.
6. (a) What steels can be tempered?
   (b) What compound is found in all steels at high temperatures? What is its formula?
   (c) What is meant by the quenching of steel? How does this process affect the properties of steel?
   (d) What is meant by the tempering of steel? Discuss the effect of this process on the properties of steel.
7. (a) What is an alloy steel?
   (b) Name five alloy steels and mention one property and one use of each.

CHAPTER XLIV

ALUMINUM

1. Occurrence

Aluminum is the most abundant of all the metallic elements found in the earth's crust and the third most abundant of all the chemical elements. Unlike some metals, such as gold or copper, aluminum is never found in nature in the free state. It is always found in chemical combination with other elements, and its chief compounds are the silicates and oxides. *Clay* and nearly all of our common rocks contain some aluminum, yet the cost of obtaining the metal from these sources is so high that at present it is produced in Canada from only one mineral, bauxite, which is rich in aluminum. *Bauxite* is a mixture consisting chiefly of hydrated aluminum oxide, $Al_2O_3.2H_2O$, and ferric oxide, Fe_2O_3. It is the most important aluminum ore, and it is found in France, British Guiana, Arkansas, Alabama and Georgia. *Cryolite*, Na_3AlF_6, a word of Greek origin meaning *ice-stone*, is found in commercial quantities only in Greenland. It is needed in the production of aluminum from bauxite. The mineral corundum is chiefly aluminum oxide, Al_2O_3. *Emery*, which is an extremely useful and important natural abrasive, is



Courtesy of Aluminum Co. of Canada, Ltd.

FIG. 174—MINING BAUXITE IN BRITISH GUIANA

an impure variety of Al_2O_3. *Sapphires* and *rubies*, which are valuable gems, consist chiefly of crystallized aluminum oxide.

2. Preparation: Hall's Process

Since aluminum is very active chemically, its oxide cannot be reduced to the free element by means of carbon in a furnace. The metal was first prepared in 1825 by Oersted, a Danish scientist, who reduced aluminum chloride with metallic potassium.

$$AlCl_3 + 3\ K \longrightarrow Al + 3\ KCl$$

Other scientists devised chemical processes for reducing aluminum ores, but they were complicated and expensive. The metal sold for about $500 a pound in 1852. Seven years later improvements in the methods of production brought the price down to $17 a pound, but it was still classed as a "precious" metal.

The story of the discovery of an economical method for extracting aluminum from its ores is a most interesting one. In 1886 Charles Martin Hall, a 22-year-old Ohio boy, discovered the electrolytic process of reducing aluminum from its oxide. He became interested in the problem of securing aluminum from its ores when he was a student at Oberlin College, which is located at Oberlin, Ohio. After graduating from College he continued his experiments in his father's woodshed, where he found that molten cryolite (a sodium aluminum fluoride mineral) would dissolve aluminum oxide, and so make it possible to pass an electric current through the solution. It is interesting to know that the large-scale process of securing aluminum today is practically the same as the one devised by the young American chemist.

Hall's process is essentially the electrolysis of pure aluminum oxide, Al_2O_3, dissolved in molten cryolite, Na_3AlF_6, which serves as the electrolyte. The pure Al_2O_3 is obtained from bauxite ore by a method known as the Bayer process. The details of this method are beyond the scope of this text. It takes about two pounds of bauxite to produce one pound of alumina (Al_2O_3).

The details of the electrolytic reduction of the oxide to the free metal are given below.

(1) The reduction takes place in an electrolytic cell constructed of iron and lined with carbon which serves as the cathode (negative).

(2) Large carbon rods (see Fig. 175) serve as anodes (positive).

(3) The cryolite is first placed in the cell and then the electric

current is turned on. The resistance of the cryolite to the passage of the electric current produces enough heat to melt it. (4) The pure aluminum oxide, Al_2O_3, obtained from bauxite is now added. It dissolves in the molten cryolite and, as the current passes through the molten solution, metallic aluminum is deposited at the cathode. It sinks to the bottom of the box

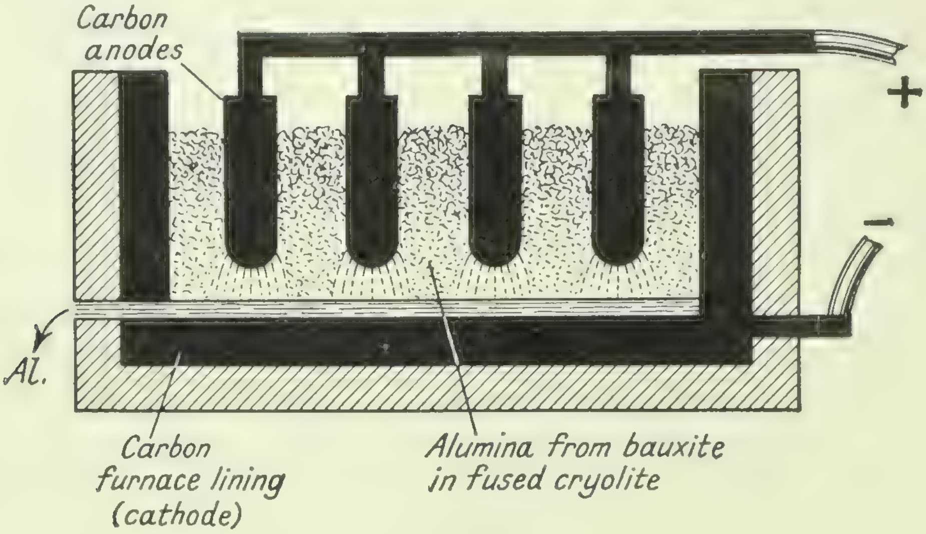
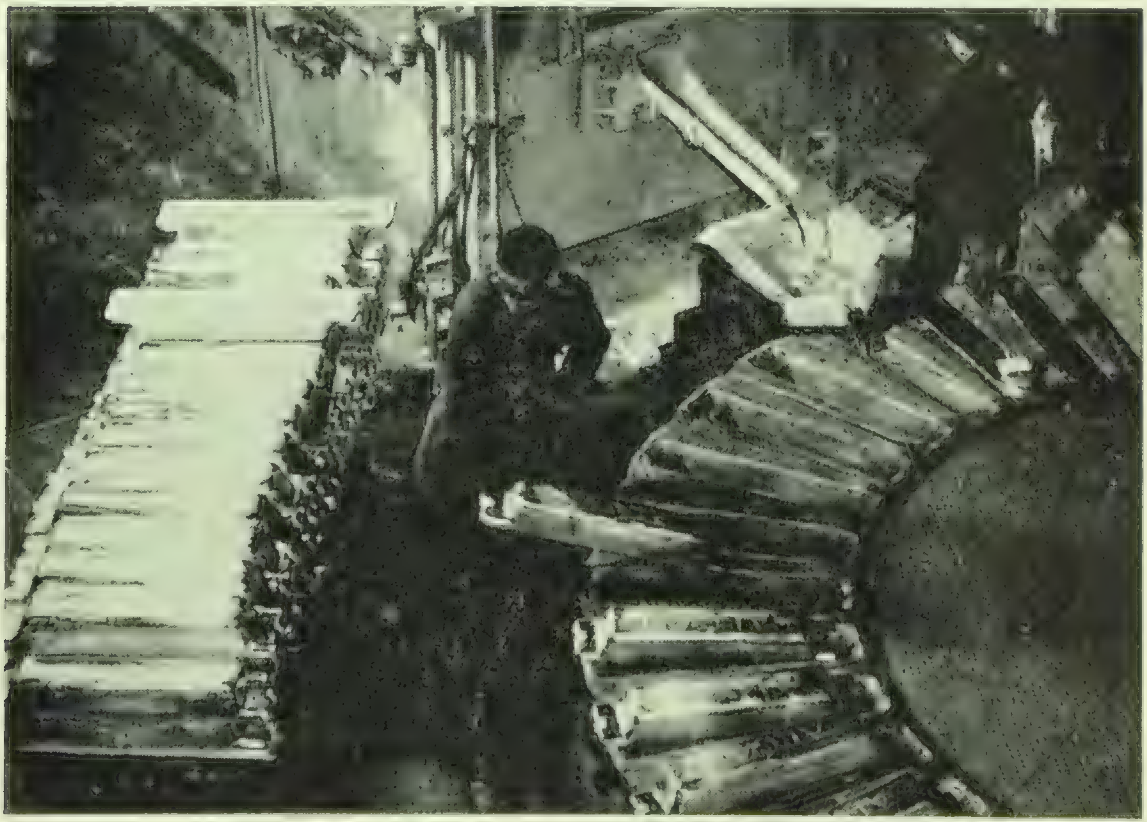

Carbon anodes
+
−
Al.
Carbon furnace lining (cathode)
Alumina from bauxite in fused cryolite

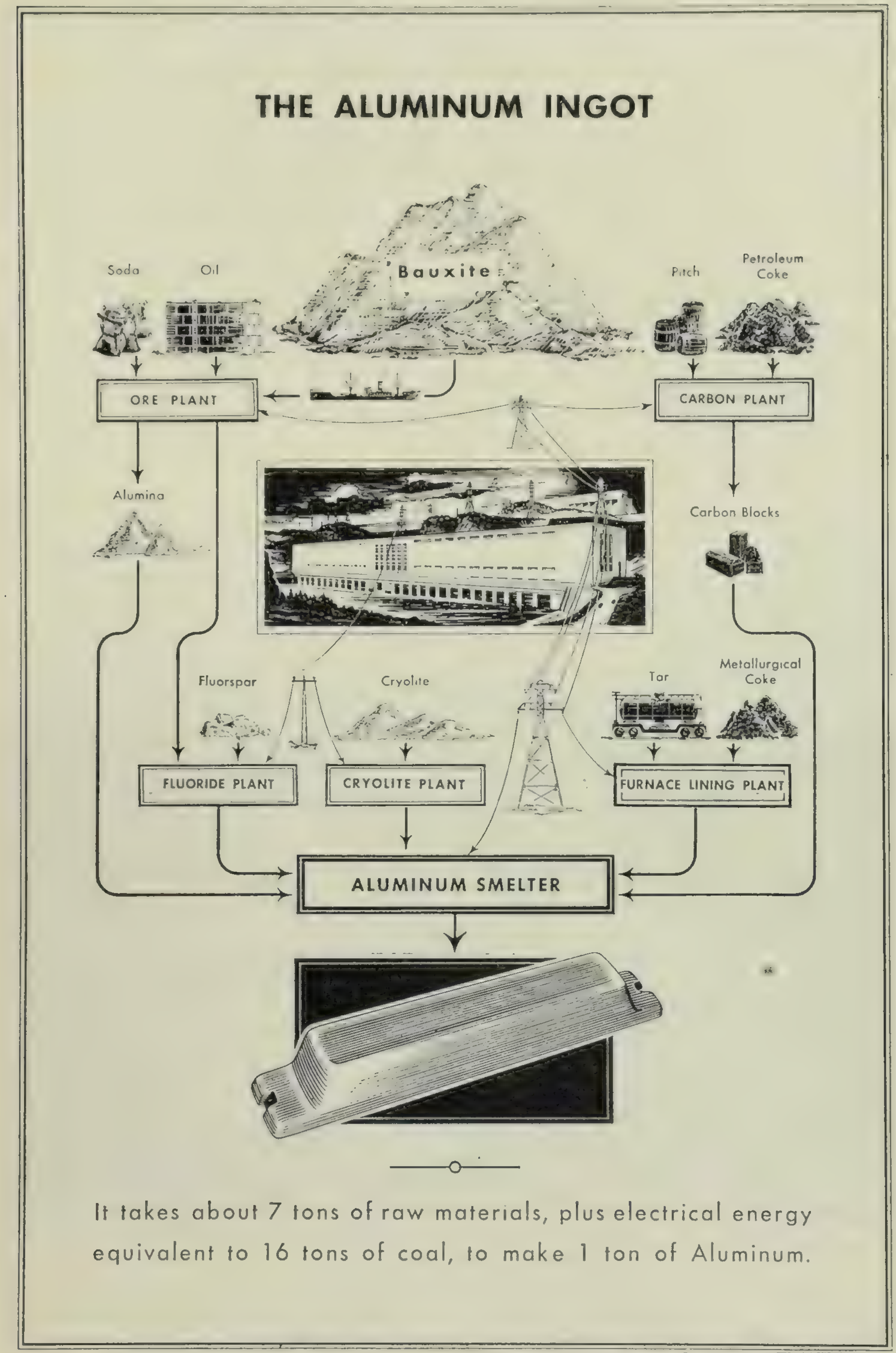
FIG. 175
MANUFACTURE OF ALUMINUM BY THE ELECTROLYSIS OF PURE ALUMINUM OXIDE (ALUMINA), DISSOLVED IN FUSED (MOLTEN) CRYOLITE



Courtesy of Aluminum Co. of Canada, Ltd.

FIG. 176—POURING ALUMINUM INTO INGOTS ON TURNTABLE

while the oxygen, liberated at the anodes, combines with the carbon forming carbon monoxide and carbon dioxide. These



THE ALUMINUM INGOT

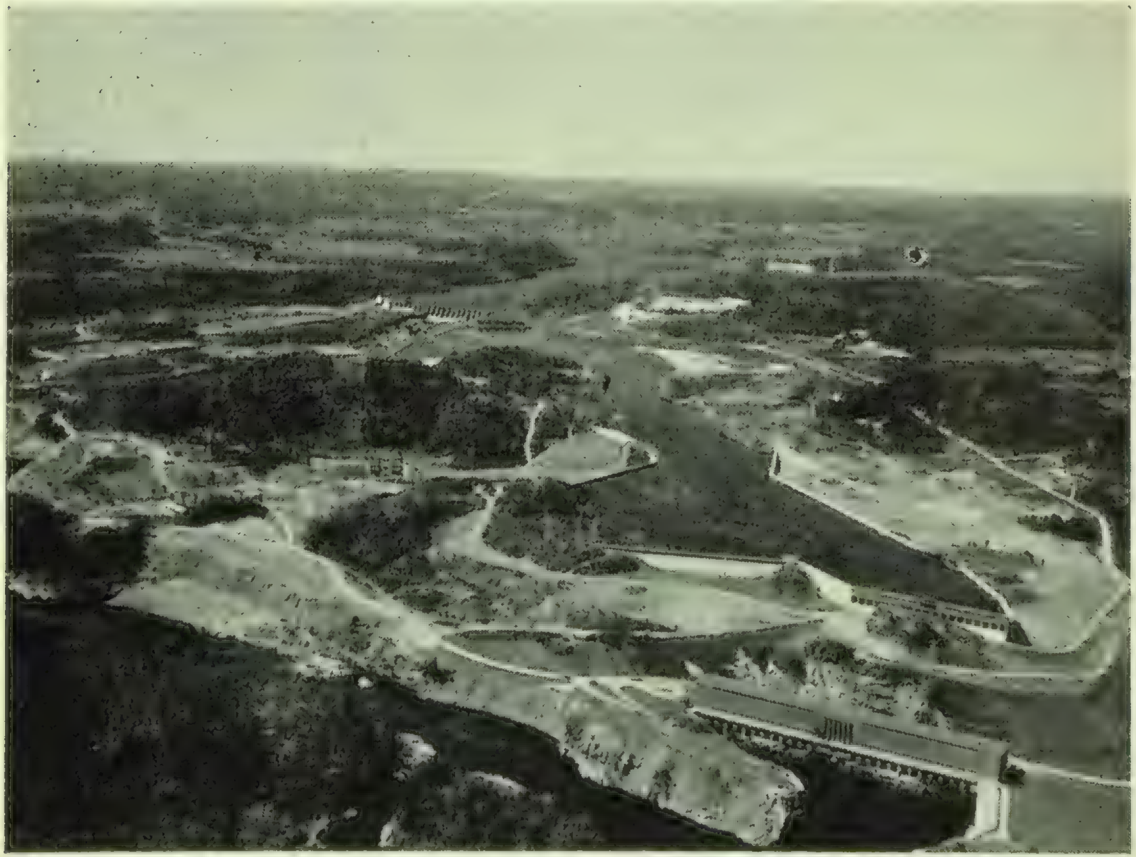
It takes about 7 tons of raw materials, plus electrical energy equivalent to 16 tons of coal, to make 1 ton of Aluminum.

Courtesy of Aluminum Co. of Canada, Ltd.

FIG. 177

gases escape from the anodes into the air. The oxidation of the carbon rods makes necessary their replacement by new ones quite often, and this has been one disadvantage to the process. (5) The molten layer of aluminum, from time to time, is drawn off from the bottom of the cell into large ladles and cast into pigs. The process is continuous. As the aluminum oxide in the cryolite bath becomes used up, more oxide is added so that the reactions at the electrodes go on without any interruptions.

The metal, which is obtained from the electrolytic cell, contains some impurities, and so pig aluminum is not suitable for most industrial purposes. It is remelted and the impurities removed. The molten metal is then cast into ingots for commercial use, as shown in Fig. 176. Its aluminum content is over 99.5 per cent with iron and silicon as the chief impurities. Fig. 177 shows the production of aluminum ingot from bauxite to the finished product.



Courtesy of Aluminum Co. of Canada, Ltd.

FIG. 178

The Shipshaw power development with Shipshaw No. 2 in the foreground and Shipshaw No. 1 in the background. The canal between the two powerhouses much of which was dug through solid rock, is 1½ miles long. The total generating capacity is 1,500,000 horse power. Shipshaw No. 1 was completed in 1931 and Shipshaw No. 2 in 1943.

Canada has no bauxite deposits and also lacks all or nearly all of the other basic materials needed in the production of aluminum. However, Canada does possess abundant electrical energy, essential for the production of aluminum. For this reason, most of the aluminum is produced at Arvida, Quebec, and Shawinigan Falls, Quebec, where huge quantities of low-cost hydro-electric power are available. Fig. 178 shows the Shipshaw power development which can generate 1,500,000 horse power of electrical energy.

3. Physical Properties

(1) Aluminum is a silvery, white metal, resembling tin in appearance.
(2) It is the lightest of the common metals. Its density is 2.7, about one-third that of iron and about the same as that of glass.
(3) Like most metals aluminum is malleable and ductile.
(4) Aluminum is a good conductor of heat and electricity.
(5) It is fairly hard and strong, being superior to most metals in these respects, although not equal to steel.
(6) The metal melts at 660° C. (1220° F.)

4. Chemical Properties

(1) Aluminum combines with the oxygen of the air at ordinary temperatures only until a thin coating of aluminum oxide is formed. This film, about .0000004 inches in thickness, protects the metal underneath it from further oxidation. The interesting thing about this film of oxide is that it is self-healing, so that, if the surface is scratched and the film broken, the exposed aluminum at once combines with more oxygen of the air to form a fresh film. This fact makes the metal resistant to most kinds of chemical attack. At 600° C., and even above that temperature, combination of aluminum with oxygen is still somewhat slow, except in the case of the very fine powder. However, at high temperatures, the element burns with a very brilliant flame.

$$4\ Al + 3\ O_2 \longrightarrow 2\ Al_2O_3$$

(2) The metal does not react with water, even though it is a fairly active metal. The formation of aluminum oxide on the surface of the metal prevents reaction with water.
(3) It reacts readily with dilute hydrochloric acid producing hydrogen.

$$2\ Al + 6\ HCl \longrightarrow 2\ AlCl_3 + 3\ H_2\uparrow$$

(4) It is a powerful reducing agent. For example, it can reduce ferric oxide to free iron with the liberation of enough heat to produce a temperature of about 3000°C.

$$2\ Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2\ Fe$$

5. Uses

(1) The first important use of aluminum was for making cooking utensils. This use is based upon the fact that the metal is a good conductor of heat.

(2) It is used extensively as a conductor for electrical power transmission lines. The electrical conductivity of aluminum is about 65 per cent that of copper, but because of its low density it competes successfully on a weight basis with that metal. More than one million miles of aluminum cable in power lines are now in use. The wire contains a core of steel which gives it greater strength.

(3) Because of its lightness and strength, aluminum is used in the construction of automobiles, aircraft, and trains.

(4) Aluminum foil is used to a considerable extent in the packaging of materials.

(5) It is very useful as a decorative and structural metal for architectural purposes. An example of such a use is shown in Fig. 179.

(6) When aluminum is mixed with oil, a so-called "silver paint" is produced. This material is used to cover metal objects or to make silver screens for the showing of films.

(7) Aluminum is used in the manufacture of iron and steel to remove oxygen. This prevents blow-holes in the castings.

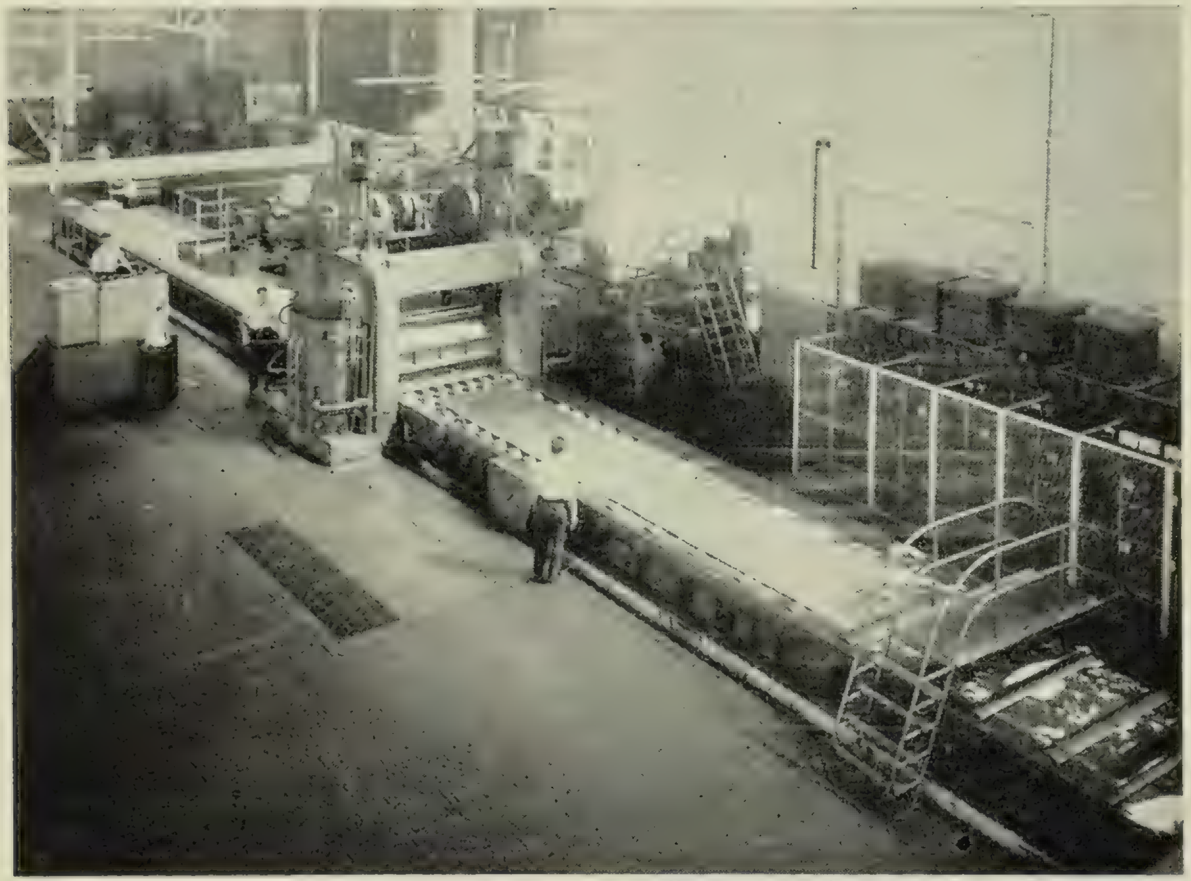
(8) It is used in the production of an explosive, known as *ammonal*, which is a mixture of powdered aluminum and ammonium nitrate.

Courtesy of Aluminum Co. of Canada, Ltd.

FIG. 179—A CLOSE-UP VIEW OF AN ALUMINUM STAIR BANNISTER IN A LARGE OFFICE BUILDING

(9) Because aluminum is such a powerful reducing agent, it is used in the so-called *Goldschmidt process* for welding. Ferric oxide and aluminum, both as coarse powders, are mixed to-

gether to form a mixture, known as *thermit.* This material is well suited to repair broken iron objects, such as steel rails. The broken part is covered with thermit, which is ignited by means of a special fuse (Mg, $KClO_3$). The heat produced by the burning of the fuse starts the reduction of the ferric oxide by the aluminum powder, producing a temperature of about 3000° C. in 60 seconds. This very high temperature melts the iron, which flows into the crack or break and welds together the broken parts. Thermit is also one of the materials used in incendiary bombs.



Courtesy of Aluminum Co. of Canada, Ltd.

FIG. 180—ALUMINUM SHEET ROLLING MILL. THE SHEETS ARE USED TO MANUFACTURE MANY FAMILIAR ARTICLES

6. Some Important Alloys of Aluminum

In the aluminum alloys certain properties of pure aluminum are changed to a considerable extent. For example, strength is greatly improved. Some properties of aluminum remain practically unchanged. The most outstanding of these is the property of lightness. With few exceptions, the increase in density of the aluminum alloys over that of pure aluminum does not exceed 3 per cent, while several alloys are slightly lighter than the pure metal. On the other hand, the electrical conductivity is decreased to a considerable extent when another metal is mixed with aluminum. It is interesting to know that about half the aluminum produced in industry is used to form alloys. A few important aluminum alloys will be considered below.

(1) DURALUMIN. This is one of the most important alloys of aluminum. It contains about 4 per cent copper, about 0.5 per cent each of manganese and magnesium, and 95 per cent aluminum. The tensile strength of this alloy is about the same as that of medium steel, or about twice that of pure aluminum. Duralumin is almost as light as pure aluminum and it resists corrosion. It takes a high polish and it can be cast into moulds.

Duralumin possesses the lightness of aluminum and the strength of steel, and so it is used considerably in aeroplane and dirigible construction. More than 60 per cent of the structural part of an aircraft is aluminum, and millions of pounds of this metal were used during World War II in the production of war planes. In the manufacture of steel railway cars a decrease in weight of about 13,000 pounds per car has been accomplished by the use of duralumin. Duralumin has completely replaced wood and steel in the construction of some auto-buses. This has meant a decrease of about a ton in the weight of the bus, and so less gasoline is needed to operate it.

(2) MAGNALIUM. This alloy contains from 10 to 25 per cent magnesium and the rest is aluminum. It is lighter than pure aluminum and is quite rigid. Magnalium can be turned in a lathe and is used in making laboratory balances.

(3) ALUMINUM BRONZE. This is an alloy of copper containing not more than 11 per cent aluminum. It is hard, elastic, and strong. Aluminum bronze takes a high polish and it is easily cast and worked. It is used to make automobile crank cases, connecting rods and many other parts.

7. Some Important Compounds of Aluminum

(1) ALUMINUM OXIDE, Al_2O_3. Aluminum oxide is found in nature as the mineral *corundum*, which is next to the diamond in hardness. *Emery* is an impure form of corundum. For many years these two substances have been used as *abrasives*. An artificial material, known as *alundum*, which is also aluminum oxide, is produced from bauxite. This substance is used as an abrasive as well as in the manufacture of crucibles, tubes and other kinds of chemical apparatus. The *ruby*, *sapphire*, *topaz*

and a few other gems are crystalline aluminum oxide, coloured by small quantities of metallic substances. Synthetic gems such as those mentioned above can now be produced by melting corundum in the oxy-hydrogen blowpipe. The composition and properties of these synthetic gems are almost the same as the natural stones.

(2) ALUMINUM HYDROXIDE, $Al(OH)_3$. When ammonium hydroxide is added to a solution of a soluble aluminum salt, a white, gelatinous precipitate is formed. It is aluminum hydroxide, $Al(OH)_3$.

$$Al_2(SO_4)_3 + 6\ NH_4OH \longrightarrow 2\ Al(OH)_3\downarrow + 3\ (NH_4)_2SO_4$$

When dilute acids are added to aluminum hydroxide, it dissolves forming the aluminum salt of the acid used.

$$Al(OH)_3 + 3\ HCl \longrightarrow AlCl_3 + 3\ H_2O$$

On the other hand, a solution of a strong base, such as sodium hydroxide, will also dissolve a precipitate of aluminum hydroxide. The reason for this is that aluminum hydroxide is converted to a weak acid, $HAlO_2 . H_2O$, in the presence of a strong base. This acid reacts with the base to form a soluble salt, known as an *aluminate*.

$$Al(OH)_3 \rightleftharpoons HAlO_2 . H_2O$$

$$HAlO_2 . H_2O + NaOH \longrightarrow \underset{\text{(sodium aluminate)}}{NaAlO_2 . H_2O} + H_2O$$

A substance, like aluminum hydroxide, which can behave as an acid or a base depending upon the conditions, is said to be *amphoteric*.

Aluminum hydroxide has several important uses, most of which are due to its ability to *adsorb* other materials. If it is precipitated in a suspension of clay in water, the gelatinous precipitate, $Al(OH)_3$, adsorbs and carries down with it the suspended material. This fact is made use of in the purification of water. In practice, alum and aluminum sulphate, which are hydrolyzed (decomposed) by water to give aluminum hydroxide, are used extensively for this purpose.

Aluminum hydroxide is also used as a *mordant* in the dye industry. Mordants are substances which serve to bind the dye to the textile, especially in the case of cotton and linen. Some dyes do not adhere to the textile fibre, but are adsorbed by the mordant, which holds fast to the cloth. Thus, the dye is attached firmly to the textile. This would be impossible without the aid of the go-between (the mordant).

The Alums—Aluminum Sulphate.

Alums are double salts. The most common one, *potassium alum* (ordinary alum), has the following formula:

$$K_2SO_4 . Al_2(SO_4)_3 . 24\ H_2O$$

The formula for ammonium alum is:

$$(NH_4)_2SO_4 . Al_2(SO_4)_3 . 24\ H_2O$$

These two alums are white, crystalline substances with an astringent taste. Chrome alum, which is purple in colour, has the formula:

$$K_2SO_4 . Cr_2(SO_4)_3 . 24\ H_2O$$

Ferric alum is:

$$(NH_4)_2SO_4 . Fe_2(SO_4)_3 . 24\ H_2O$$

The *normal sulphate*, $Al_2(SO_4)_3 . 18\ H_2O$, can now be prepared with a fairly high degree of purity and it is replacing ordinary alum for most purposes. Aluminum sulphate has many industrial uses. We have already mentioned its use for furnishing aluminum hydroxide in *water purification*, and it is also used to supply the hydroxide as a mordant in *dyeing*. Much aluminum sulphate is used in the *sizing of paper*, and it is also used in the *fixing bath* in photographic work.

EXERCISES

1. Write a note on the occurrence of aluminum.
2. Discuss Hall's Process for the production of aluminum. Illustrate your answer with a labelled diagram.
3. Discuss briefly why the aluminum industry is located in Canada.
4. Tabulate five physical properties of aluminum and give one use due to each property.
5. Discuss carefully the chemical property of aluminum which enables it to resist corrosion so well.
6. Tabulate five chemical properties of the metal and point out a possible use due to each property.
7. Write a note on thermit.
8. (a) Discuss the advantages of aluminum alloys as compared to pure aluminum.
   (b) Write a note on any one of the following; duralumin, magnalium, aluminum bronze.
9. Tabulate the various forms of aluminum oxide and give one use of each.
10. Aluminum hydroxide is said to be amphoteric. Discuss this statement carefully, using equations to illustrate your answer.
11. Write a note on the uses of aluminum hydroxide.

12. (a) What is an alum?
  (b) Write the names and formulas for three.

13. (a) What is the formula for normal aluminum sulphate?
  (b) Write a brief note on the uses of this compound.

Chapter XLV

ORGANIC CHEMISTRY: THE HYDROCARBONS

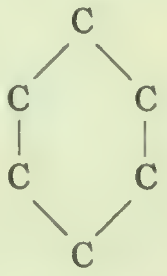
1. What is Organic Chemistry?

The *hydrocarbons* are *organic* compounds which, as the name suggests, contain the elements hydrogen and carbon. Before making a study of these important compounds, we shall consider what is meant by the term organic chemistry. It can be defined as that branch of chemistry which deals with the carbon compounds. The pioneer organic chemists believed that only some living *organism*, a plant or an animal, could produce carbon compounds; hence the name organic was applied to these compounds. The chief elements found in organic compounds are carbon, hydrogen, and oxygen. A few organic substances contain sulphur, nitrogen and phosphorus. For example, all proteins contain nitrogen, in addition to carbon, hydrogen, and oxygen.

Carbon compounds are very numerous. Organic chemists tell us that there are about 300,000 carbon compounds at the present time, and methods of preparing new ones are being discovered every year. No other element has the property of forming so many compounds. The number of compounds which do not contain carbon are only about 27,000. There are so many carbon compounds because the atoms of this element have the ability to combine with themselves to form chains and rings. For example, six carbon atoms form the skeleton chain of the hexane molecule.

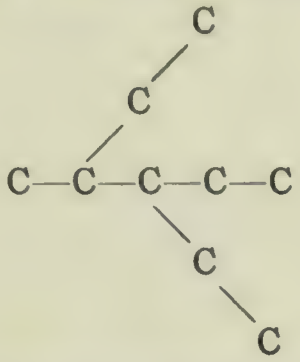
$$\underset{\text{(six carbon atoms)}}{C + C + C + C + C + C} \longrightarrow \underset{\text{(hexane chain)}}{C—C—C—C—C—C}$$

Again, six carbon atoms make up the benzene ring.



(benzene ring)

These chains contain from 2 to 60 or more atoms, and in addition, a normal chain may have side chains as shown below.



(Carbon chain with side chains)

Organic compounds play a very important part in our lives. Textiles, foods, fuels, drugs, dyes and explosives are a few examples of organic materials which are so essential to modern civilization. Our bodies are made up, for the most part, of organic compounds; therefore, medical scientists must have a knowledge of organic chemistry. Many of our industrial developments, such as nylon and plastics, are due to the researches of organic chemists.

Since there are so many organic compounds it is necessary to classify them into groups or families. A few of the chief groups are:

1. Hydrocarbons
2. Alcohols
3. Ethers
4. Aldehydes and Ketones
5. Acids
6. Esters
7. Fats
8. Carbohydrates
9. Proteins

2. The Hydrocarbons.

The hydrocarbons, compounds of hydrogen and carbon, make up an important group of organic compounds. Hydrocarbons occur quite widespread in nature. They are found in petroleum (crude oil), and the numerous products obtained from that substance. Gasoline, kerosene, lubricating oils, vaseline and paraffin, are a few of the more important materials secured from petroleum. Natural gas is composed chiefly of the simplest of all hydrocarbons, methane (CH_4). Many important hydrocarbons are obtained from coal-gas and coal-tar. All plants contain hydrocarbons, and those produced by some plants are of great industrial importance. Rubber and turpentine are two outstanding examples of such compounds.

The hydrocarbons can be classified into four series:

1. The Methane (Paraffin) Series
2. The Ethylene Series
3. The Acetylene Series
4. The Benzene Series

The members of each series have the same general properties and their molecules have the same type of structure.

The *methane series* is also known as the *paraffin series* because some of the higher members are found in paraffin. The formulas and names of the simplest members, along with those of a few of the higher members of this series, are given below.

CH_4	Methane	Gases
C_2H_6	Ethane	
C_3H_8	Propane	
C_4H_{10}	Butane	
C_5H_{12}	Pentane	Liquids
C_6H_{14}	Hexane	
C_7H_{16}	Heptane	
C_8H_{18}	Octane	
C_9H_{20}	Nonane	
$C_{10}H_{22}$	Decane	
$C_{17}H_{36}$	Heptadecane	
$C_{60}H_{122}$	Hexacontane	Solid

Careful examination of the above formulas shows that each hydrocarbon molecule contains twice as many hydrogen atoms, plus two, as carbon atoms. Thus, a general formula can be written for this series: $C_nH_{2n\,+\,2}$, where n represents the number of carbon atoms in the molecule, and the number of hydrogen atoms is $2n + 2$. For example, propane contains 3 carbon atoms in its molecule and twice this number of hydrogen atoms plus 2, which is 6, and so the formula of propane is C_3H_8. It will also be observed that the molecule of one hydrocarbon differs from the one next to it in the series by one atom of carbon and two atoms of hydrogen (CH_2). Whenever we have a series of compounds where the difference between any two adjacent members is CH_2, the series is known as an *homologous* series. The word "homologue" means "a member of the series." Homologous series are encountered quite often in organic chemistry, and the student should remember that other families besides the hydrocarbons contain such series of compounds.

It is well to remember that members of an homologous series possess strong chemical resemblances. They do not show exactly the same chemical properties, but they do have some common chemical characteristics which enable us to distinguish them from other classes of compounds.

The *ethylene* series has the general formula C_nH_{2n}. The formulas and names of a few of the simplest members of this series are given below.

C_2H_4	Ethylene	Gases
C_3H_6	Propylene	
C_4H_8	Butylene	
C_5H_{10}	Amylene	Liquid

Again, it is observed that these compounds make up an homologous series, just as the paraffins, because there is the same difference between any two consecutive members of CH_2. Of course, it will be observed that the members of this series have two hydrogen atoms less per molecule than the corresponding members of the methane series. In naming these compounds, it will be noticed that the ending *ane* of the paraffins is changed to *ylene* in the ethylene series.

The general formula for the *acetylene series* is C_nH_{2n-2}. The names and formulas for the first three members of this series are given below.

C_2H_2	Acetylene
C_3H_4	Methylacetylene
C_4H_6	Dimethylacetylene

This is also an homologous series. The members of this series have two hydrogen atoms less than the corresponding members of the ethylene series, or four hydrogen atoms less than the corresponding members of the methane series. This series is called the acetylene series, because acetylene is the most important member.

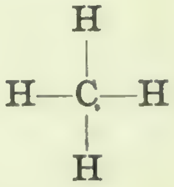
The general formula for the *benzene series* is C_nH_{2n-6}. The names and formulas of three members of this series are given below.

C_6H_6	Benzene
C_7H_8	Toluene
C_8H_{10}	Xylene

Again, it is noticed that this is an homologous series. It is known as the benzene series because all members of it can be prepared from benzene.

3. Methane, CH_4

This is the simplest member of the methane or paraffin series of the hydrocarbons. Organic chemists soon found that molecular (ordinary) formulas were not satisfactory for explaining the reactions of organic compounds, and so they devised structural formulas. The structural formula for methane is shown below.



$$\begin{array}{c} H \\ | \\ H—C—H \\ | \\ H \end{array}$$

T. N. T.

The decay of vegetable material produces methane, and it is often found coming off from swamps or marshes. For this reason, it is sometimes known as "marsh gas." Methane makes up a large proportion of natural gas (80 per cent or more). It is also found in coal gas (30-40 per cent). Fires and explosions in coal mines are chiefly caused by the combustion of a mixture of methane and air, and so methane is also called "fire-damp." Damp is an old English word for gas.

Methane may be made from its elements by passing hydrogen over carbon at 475° C. in the presence of nickel, which serves as a catalyst.

$$C + 2\ H_2 \longrightarrow CH_4$$

The laboratory method consists of heating a mixture of anhydrous sodium acetate and soda lime (NaOH + CaO).

$$\underset{\text{(sodium acetate)}}{CH_3\cdot\boxed{COONa + NaO}}H \longrightarrow CH_4\uparrow + Na_2CO_3$$

Sodium acetate is the sodium salt of acetic acid, and it reacts according to the above equation with the sodium hydroxide. The calcium oxide prevents the mixture from forming a hard mass during the heating, and it plays no part in the chemical reaction. The formation of a solid mass would hinder rapid escape of the methane.

Methane is a colourless gas with a slight odour. It burns with an almost non-luminous flame.

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$$

It is important to remember that all hydrocarbons burn to give carbon dioxide and water. This reaction gives off a great deal of heat, and so methane and other hydrocarbons possess a high fuel value. It has already been mentioned that a mixture of methane and air is explosive, and this fact explains the many explosions which take place in coal mines. Methane is inactive chemically and quite stable. Methane and other members of this series are called *paraffins*, which is a contraction of the Latin words "parum affinis," which means "little affinity." Common chemical reagents, such as hydrochloric, nitric and sulphuric acids, and sodium hydroxide, do not react with methane or other members of the paraffin series.

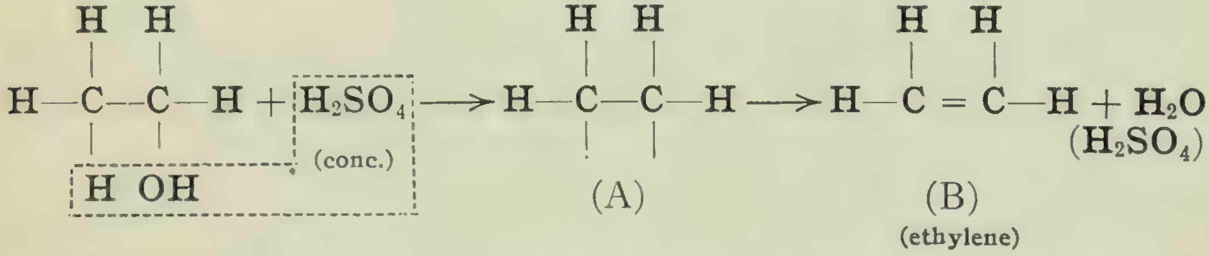
Methane is used to a very considerable extent as a fuel. It is also used in some places for lighting purposes.

4. Ethylene, C_2H_4

This is the most important member of the *ethylene* or unsaturated hydrocarbon series (C_nH_{2n}). The structure of its molecule can be explained most readily by describing first the method by which the substance is produced in the laboratory. It is prepared by heating ethyl alcohol, C_2H_5OH, with concentrated sulphuric acid. The acid removes a molecule of water from the alcohol molecule. This is expressed by an ordinary (molecular) equation as follows:

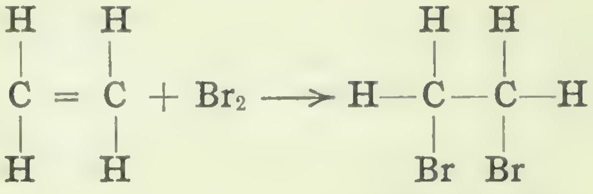
$$C_2H_5OH + H_2SO_4 \longrightarrow C_2H_4\uparrow + H_2O(H_2SO_4)$$

The organic chemist attempts to explain the above reaction by means of structural formulas as shown below.



$$\begin{array}{c}H\;\;H\\ |\;\;\;\;|\\ H-C-C-H\\ |\;\;\;\;|\\ H\;\;OH\end{array} + \underset{\text{(conc.)}}{H_2SO_4} \longrightarrow \underset{\text{(A)}}{\begin{array}{c}H\;\;H\\ |\;\;\;\;|\\ H-C-C-H\\ |\;\;\;\;|\\ \;\end{array}} \longrightarrow \underset{\text{(B) (ethylene)}}{\begin{array}{c}H\;\;\;\;H\\ |\;\;\;\;\;\;|\\ H-C=C-H\end{array}} + \underset{(H_2SO_4)}{H_2O}$$

The removal of a hydrogen atom (H) from one carbon atom and the removal of the hydroxyl radical (OH) from the other, leaves each carbon atom with one unused valence as shown by formula (A). To show that carbon has a valence of 4, the organic chemist places this unused valence bond between the two carbon atoms, which are said to be held together by a *double bond* as shown by formula (B). Compounds containing double or triple bonds are said to be *unsaturated*. This means that the molecule will form *addition* compounds by combining with atoms of active elements, such as bromine or chlorine. For example, bromine adds on to ethylene to produce ethylene bromide or dibromoethane.



$$\begin{array}{c} H \\ | \\ C \\ | \\ H \end{array} = \begin{array}{c} H \\ | \\ C \\ | \\ H \end{array} + Br_2 \longrightarrow H - \begin{array}{c} H \\ | \\ C \\ | \\ Br \end{array} - \begin{array}{c} H \\ | \\ C \\ | \\ Br \end{array} - H$$

(ethylene bromide)

Ethylene has some interesting uses. For example, it is used in the preparation of mustard gas $(C_2H_4Cl)_2S$. It is used in surgery, mixed with oxygen, as an anesthetic. Ethylene is also used to speed up the ripening of certain fruits and vegetables. Thus, citrus fruits can be picked when they are green, and exposure to air containing a small amount of ethylene, either during shipment or upon arrival, brings about the ripening process quickly. Ethylene bromide, formed by the action of bromine on ethylene, is necessary in the production of anti-knock gasoline. Ethylene is also an important component of certain gaseous fuels.

5. Acetylene, C_2H_2

This is the most important member of the acetylene series (C_nH_{2n-2}). Its structural formula shows that it contains a triple bond, and so it is an unsaturated compound.

$$H-C\equiv C-H$$

(acetylene)

It is prepared in the laboratory by the action of water on calcium carbide.

$$\underset{\text{(calcium carbide)}}{CaC_2} + 2\ H_2O \longrightarrow C_2H_2\uparrow + Ca(OH)_2$$

Acetylene is a colourless gas with a characteristic odour It is lighter than air and insoluble in water.

Acetylene is a poisonous gas and it is very explosive. The gas cannot be stored or shipped under pressure because of its explosive nature. However, it can be safely handled, if it is first dissolved in acetone (as in "prestolite" tanks). Acetylene burns with a very hot and yellow, smoky flame. If, however, it is mixed with air in a special type of burner, it gives an extremely hot flame and a very brilliant white light.

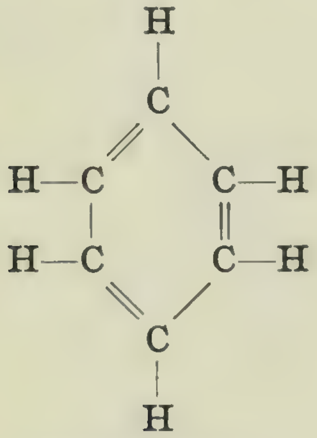
$$2\ C_2H_2 + 5\ O_2 \longrightarrow 4\ CO_2 + 2\ H_2O + \underset{\text{(calories)}}{640{,}000}$$

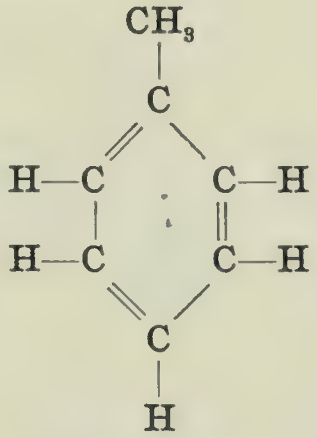
An important use of acetylene is to produce very high temperatures for welding and cutting steel by means of the oxy-acetylene blow-torch. It has been reported that a temperature of about 3000° C. can be secured by this method. It is also used in isolated places, such as mining camps, for lighting. Acetylene is used to a considerable extent in chemical industry as a starting material in the production of certain important organic compounds. For example, acetic acid can be produced from acetylene. Neoprene (duprene), one of the important synthetic rubbers, is produced from a compound called isoprene, which is made from acetylene.

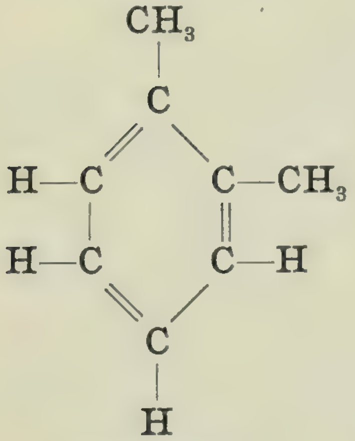
6. The Benzene Series

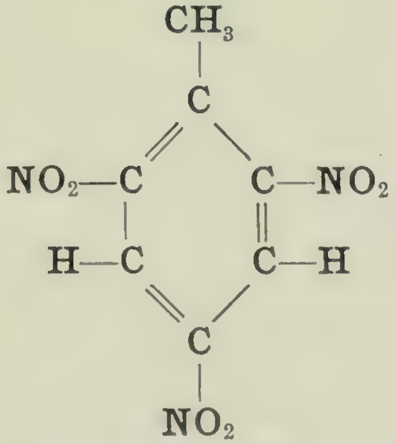
Since members of the benzene series have aromatic odours, they are also known as the aromatic hydrocarbons.

The chief source of these compounds is from the destructive distillation of coal, coal tar containing most of them. The members of this series have a closed chain or ring formation. This fact is evident upon examination of the formulas of four members of this series shown below:


benzene or benzol)


(toluene or toluol)


(xylene or xylol)


(tri-nitro-toluene, T.N.T.)

From the above formulas it is observed that three double bonds are placed in each molecule. This is necessary in order that carbon may have its normal valence of four. It must be remembered, however, that the benzene hydrocarbons are not like ethylene in their chemical properties. For example, they do not form addition compounds readily as does ethylene. They do, however, form substitution compounds quite readily. The benzene hydrocarbons are used as solvents. They are also important starting materials in the production of dyes, drugs, and explosives. For example, the powerful explosive, T.N.T., tri-nitro-toluene, $C_6H_2CH_3(NO_2)_3$, is made by treating toluene with nitric acid in a certain way. The structural formula for this compound is shown above. Benzene is used to a certain extent as a motor fuel.

EXERCISES

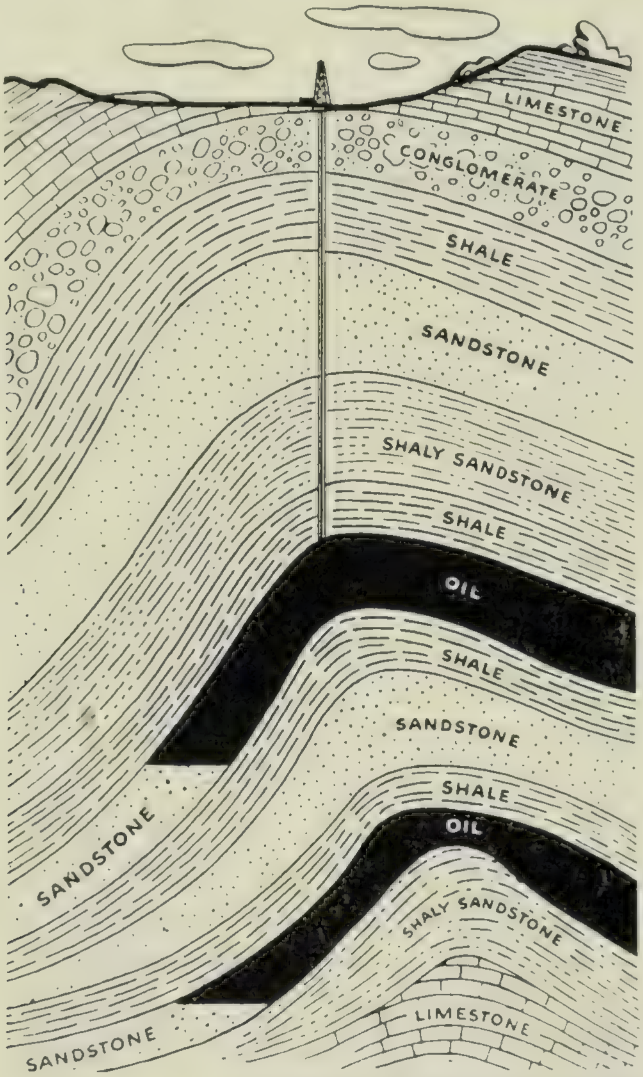
1. (a) What is organic chemistry?
   (b) What are the chief elements found in organic compounds?
2. (a) What is the approximate number of organic compounds?
   (b) Why are there so many?
3. Write a note on the importance of organic chemistry in industry and everyday life.
4. Make a list of the chief classes of organic compounds.
5. (a) What are hydrocarbons?
   (b) Write a note on the occurrence of hydrocarbons.
6. (a) What are the chief series of hydrocarbons? Give the general formula for each.
   (b) Write the names and formulas of two members of each series.
   (c) What is meant by the term homologous series?
7. Discuss methane under:
   (a) Occurrence; (b) preparation (write equation for); (c) properties; (d) uses.
8. (a) Write the structural formula for ethylene.
   (b) Distinguish carefully between saturated and unsaturated compounds.
   (c) Write a note on the uses of ethylene.
9. (a) Write the equation for the laboratory preparation of acetylene.
   (b) Tabulate the physical and chemical properties of acetylene.
   (c) Discuss its chief uses.
10. (a) What is the chief source of the benzene series of hydrocarbons?
    (b) Why do the molecules of the members of this series contain three double bonds?
    (c) Does benzene form addition compounds readily?
    (d) Write the structural formulas for:
    benzene, toluene, and T.N.T.

Chapter XLVI

PETROLEUM

1. Occurrence

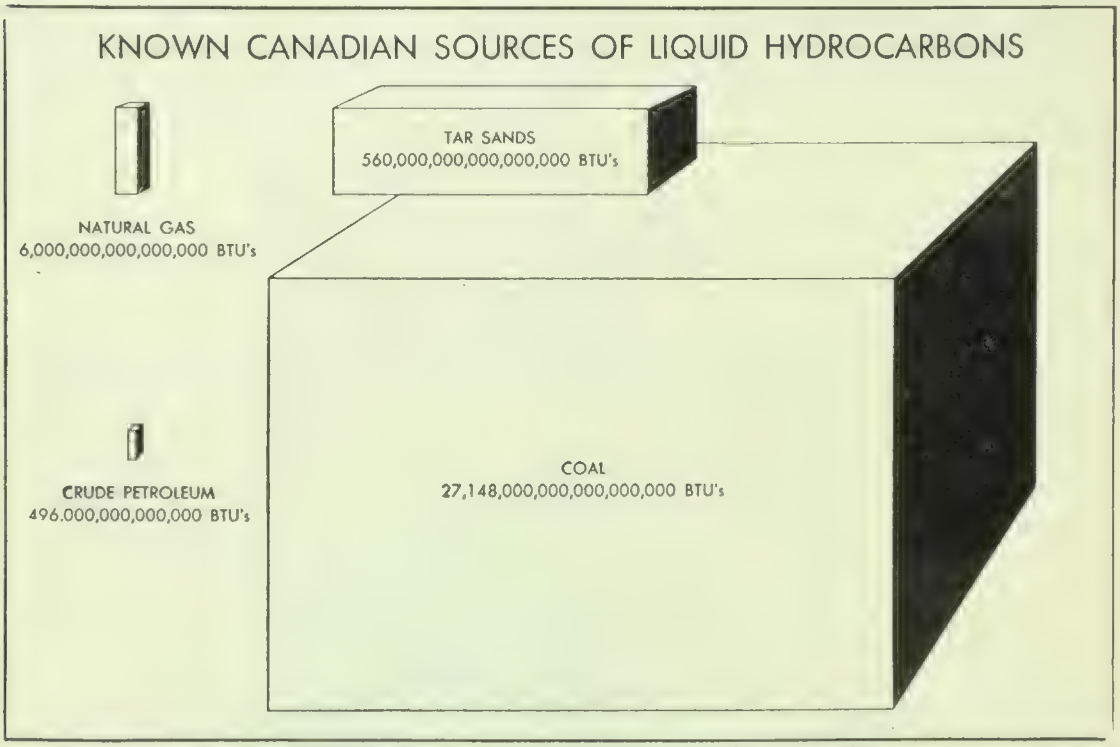
Petroleum, or crude oil, is a mixture of a large number of gaseous, liquid and solid *methane hydrocarbons*. The word "petroleum" is derived from two words *petra* and *oleum*, which mean "rock" and "oil." This is an excellent description of this liquid, which occurs in large quantities beneath the earth's surface in certain regions, as shown in Fig. 181.



Courtesy of Imperial Oil, Limited

FIG. 181—CROSS-SECTION OF EARTH STRUCTURES UNDER A PRODUCING OIL WELL

The United States is the largest producer of crude oil, supplying about 70 per cent of the world's supply. The chief oil producing states are California, Oklahoma and Texas. Other important oil producing countries are Russia, Persia (Iran), Venezuela, Rumania, Dutch East Indies and Mexico. For some years crude oil has been obtained in Canada, chiefly from the Turner Valley in Alberta. Recently a group of sub-arctic oil wells were drilled, and the oil piped about 1500 miles to a refinery which produced gasoline for planes in Alaska and trucks on the famous Alcan highway. In the Northwest, Canada has vast deposits of tar sands which may be used some day to produce gasoline (see Fig. 182).



Courtesy of Imperial Oil, Limited

FIG. 182—CANADIAN SOURCES OF LIQUID HYDROCARBONS (GASOLINE)

2. Exploration

In the past, oil fields were discovered by accident. However, most exploration for petroleum is now carried on by specially trained scientists, geologists and geophysicists, who can predict that oil may be found in a certain formation. From outcroppings of rocks on the surface a geologist can tell what the underground structure of a region is like, and so he can secure information which indicates the possibility of structures favourable to oil deposits. However, the modern geologist does not have to depend entirely upon surface geology. Science has given him certain instruments by means of which he can detect possible oil pools thousands of feet below the surface. One such instrument is the seismograph, which aids in the search for oil. Small charges of dynamite are exploded in such a way that the sound waves, from the explosion, travel down and are reflected back by underground rock formations. The returning waves are recorded by a sensitive seismograph, and the data so obtained may suggest the presence of formations favourable to the discovery of oil. Search for petroleum by means of the seismograph is conducted at sea as well as on land. For example, potential oil-producing structures have been discovered with the aid of this instrument in the Gulf of Mexico as far as 50 miles from shore. Of course, the only way to be sure that oil is present in an underground formation is to drill for it. However, it is seldom that oil is found where scientists have shown that the formations of the earth do not suggest its presence.

3. Drilling and Transportation

Modern oil well drilling is a very efficient business. One always associates drilling for oil with the *derrick*, which is constructed of wood or steel, and is usually about 150 feet in height. The base, about 30 feet in width, is wider than the top, and it must be strong and well built, because from it are suspended the heavy drilling tools, often weighing as much as 1,000,000 pounds.

There are two methods of drilling an oil well in use at present. In the older one, the work is done by means of a string of heavy tools suspended on a cable; this method is known as the *cable method*. The drilling consists of lifting these tools some distance up the well and then allowing them to drop upon the rock below. They twist upon falling, powdering or churning everything beneath. In the modern method, a *rotary rig* is used. As the name of this method suggests, the drilling tool is rotated continuously; it forces its way down through the substances underneath it in place of being carried up and dropped. In both methods the chief drilling tool is the *bit*, which bites its way into the earth or bores its way in as it twists.

As the drilling process is carried on, the waste material produced by the drill bit as it bores through the earth's crust, must be taken out of the well. In addition, the sides of the well must be made stronger to prevent the earth and rock from caving in. One method, which has been successful in carrying this crushed rock and earth up to the surface, consists of pumping through the drill pipe a special type of artificial mud, developed by petroleum engineers and chemists. This suspension, known as "drilling fluid," comes out through holes in the bit and is forced up through the space between the drill pipe and the walls of the well to the surface. This method not only sweeps up the cuttings from the drill bit, but it also keeps the turning bit lubricated and cool. The mud also serves to hold up the walls of the well to keep them from caving in. However, for this purpose it has been found better to lower down into the drill hole long pieces of steel piping. It is interesting to know that oil wells vary in depth from a few hundred feet to about nine thousand. One of the deepest wells is about ten thousand feet, which is about two miles.

When the bit goes through into the oil stratum, sometimes the pressure of gas forces the oil from the well with so much force that its flow cannot be regulated. This is known as a "gusher." Some gushers have been so powerful that they have thrown tons of drilling tools high into the air and have destroyed the derrick. Others, however, can be controlled, permitting the oil to be brought to the surface without pumping. As gushers are only encountered occasionally pumps must be used to bring the oil to the surface. The oil is conducted away from the wells in pipes and stored in enormous tanks constructed of concrete, which hold millions of cubic feet. However, metal tanks, with electrically welded joints, are gradually replacing the concrete type of storage tank. These metal containers are somewhat like oranges in appearance, having sides which are rounded and slope up and inward to come together in the centre of the top. Of course, oil men must always take special precautions against fire. As a rule, the crude oil must be transported great distances to large centres of population for refining. Tank cars, used to a limited extent, are not capable of transporting large quantities of oil quickly and at low cost. Oil tank steamers are used a great deal and, of course, this method of transportation is far cheaper than by rail. A modern device for transporting oil is the pipe line. There are over 250,000 miles of pipe lines in the United States. For example, there is one from Texas to Illinois, and there is another from Oklahoma and Kansas to the Atlantic seaboard. These pipe lines carry several million barrels of petroleum per day. Canada has two pipe lines from the United States. One comes from Illinois to Sarnia; the other starts at Portland, Maine, and comes to Montreal. The British have a pipe line from Iran (Persia) to

Haifa, a sea-port in Palestine. These pipes are about 12 inches in diameter, the sections being welded together.

4. Refining

Petroleum refining commenced many years ago when the need for kerosene arose. Gasoline was a by-product, with little commercial value, and it was usually poured into a nearby river. This practice caused serious fires, and so laws were passed to stop it. When the automobile came on the market in about 1900, gasoline became the product most in demand, as it is at the present time. This fact, along with the demand for lighter lubricating oils and for the many other substances obtained from crude oil, has caused the refining of petroleum to be a very important part of the oil industry. The refining of petroleum is a process known as *fractional distillation.* It is done in large plants called refineries, which are situated near the larger centres of population where the products obtained from the process can be sold readily. The crude oil is heated in a closed space, called a *still*, so that none of the substances which come off as gases will be lost. The escaping gases are changed to the liquid state by cooling and the resulting liquid is called a *distillate.* In the oil industry a distillate is known as a *fraction.* The fraction with the lowest boiling point escapes first, the other fractions coming off as the temperature rises. Each fraction is condensed in a separate vessel and stored by itself. The first fraction to be collected is known as *petroleum ether* and is used as a solvent. After this portion is collected, *gasoline, kerosene, gas oil*, etc., are obtained; the lighter, more volatile hydrocarbons coming off at first and then the heavier, less volatile fractions. The nature of the residue left in the still depends upon the type of crude oil used. Paraffin wax, tar, and many other substances are obtained in the refining of petroleum, as shown in Table 23.

In a refinery the fractional distillation is carried out in what oil men call a "pipe still," which contains inside it many hundreds of feet of steel pipe heated by burners inserted through one wall. The crude oil is pumped through the pipe and heated to a temperature of about 385° C. (725° F.). It then goes to the bubble tower (see Fig. 183). About every two feet up the tower there are large steel discs or trays, somewhat like pie-plates, as shown in Fig. 184. These plates contain liquid formed by condensation of some of the hot oil vapours. Fig. 184 shows

TABLE 23—PRODUCTS OBTAINED FROM CRUDE PETROLEUM BY FRACTIONAL DISTILLATION

Product	Boiling Point (0°C.)	Uses
Gases (CH_4 to C_4H_{10})		Fuel, manufacture of carbon black, manufacture of synthetic rubber.
Petroleum ether (ligroin) (C_5H_{12} to C_7H_{16})	35°-80°	In the laboratory as a solvent, dry cleaning.
Gasoline (C_5H_{12} to $C_{10}H_{22}$)	80°-200°	Motor fuel, solvent used in paint manufacturing.
Kerosene (coal oil) ($C_{11}H_{24}$ to $C_{17}H_{36}$)	200°-300°	Illumination, fuel oil.
Gas Oil	300°-380°	Cracking process to give gasoline, to enrich water gas, fuel for household furnaces, fuel for diesel engines.
Paraffin ($C_{23}H_{48}$ to $C_{27}H_{56}$) (A mixture of solid hydrocarbons, obtained from wax distillate by cooling to a low temperature. Solid wax removed by a filter press.)	melting point 52°-58°	Candles, sealing wax, waterproofing, floor wax.
Lubricating Oil ($C_{19}H_{40}$ up)	distilled with superheated steam.	Lubrication of cars, airplane engines and industrial machines.
Vaseline (a semi-solid)	distilled with superheated steam.	Lubrication, in medicine (salves), cosmetics.
Fuel oil (residue left when lubricating oil distilled off)		To preserve wood, fuel to heat industrial boilers, in manufacture of gaseous fuels.
Asphalts (tar)		Artificial asphalt, roofing, asphalt shingles, airport landing strips.
Petroleum coke		Fuel, carbon electrodes and brushes for electric motors.

how the trays work, and what takes place inside a bubble tower. The hot oil vapours rise from the tray below and bubble through the liquid in the tray above. This is the reason that this apparatus is called a "bubble tower." The light gases, escaping from the liquid, rush upward to higher trays. The heavy gases, however, are condensed and taken off in liquid form through

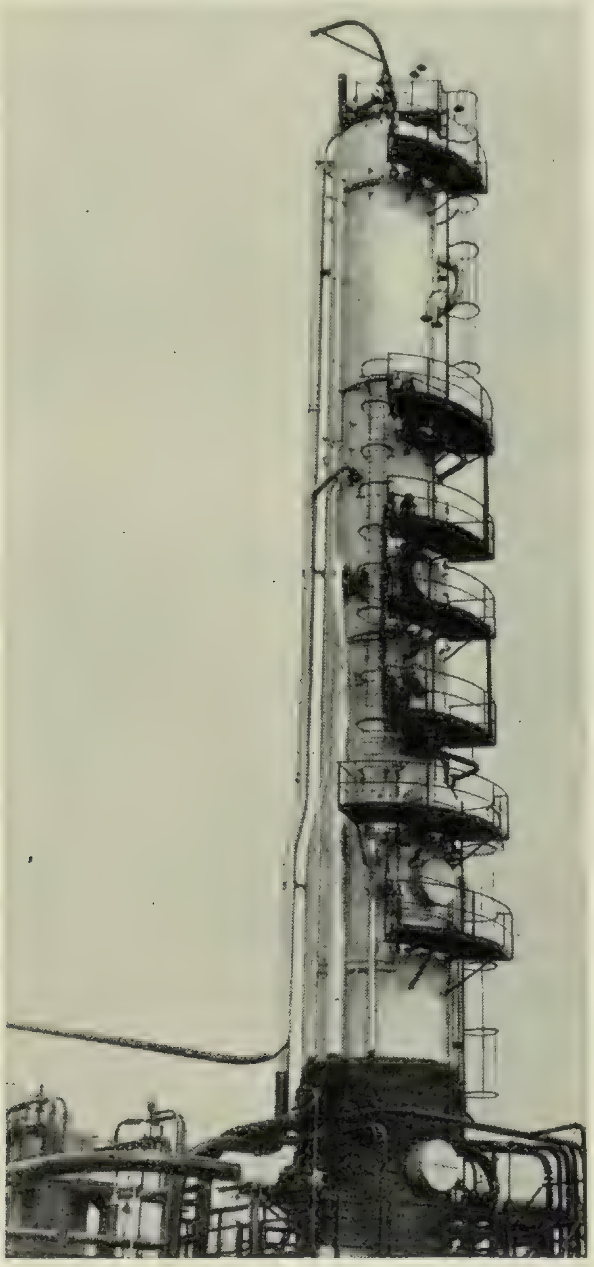


FIG. 183

A MODERN REFINING BUBBLE TOWER

It is a tall steel drum, in which the heated crude oil is separated into its various "fractions", which are drawn off through openings in the side. The bubble tower is very hot at the bottom and comparatively cool at the top.

pipes. More and more gases are changed to the liquid state as they go through the trays higher up, and the liquids so obtained are drawn off through the sides of the tower at various levels.

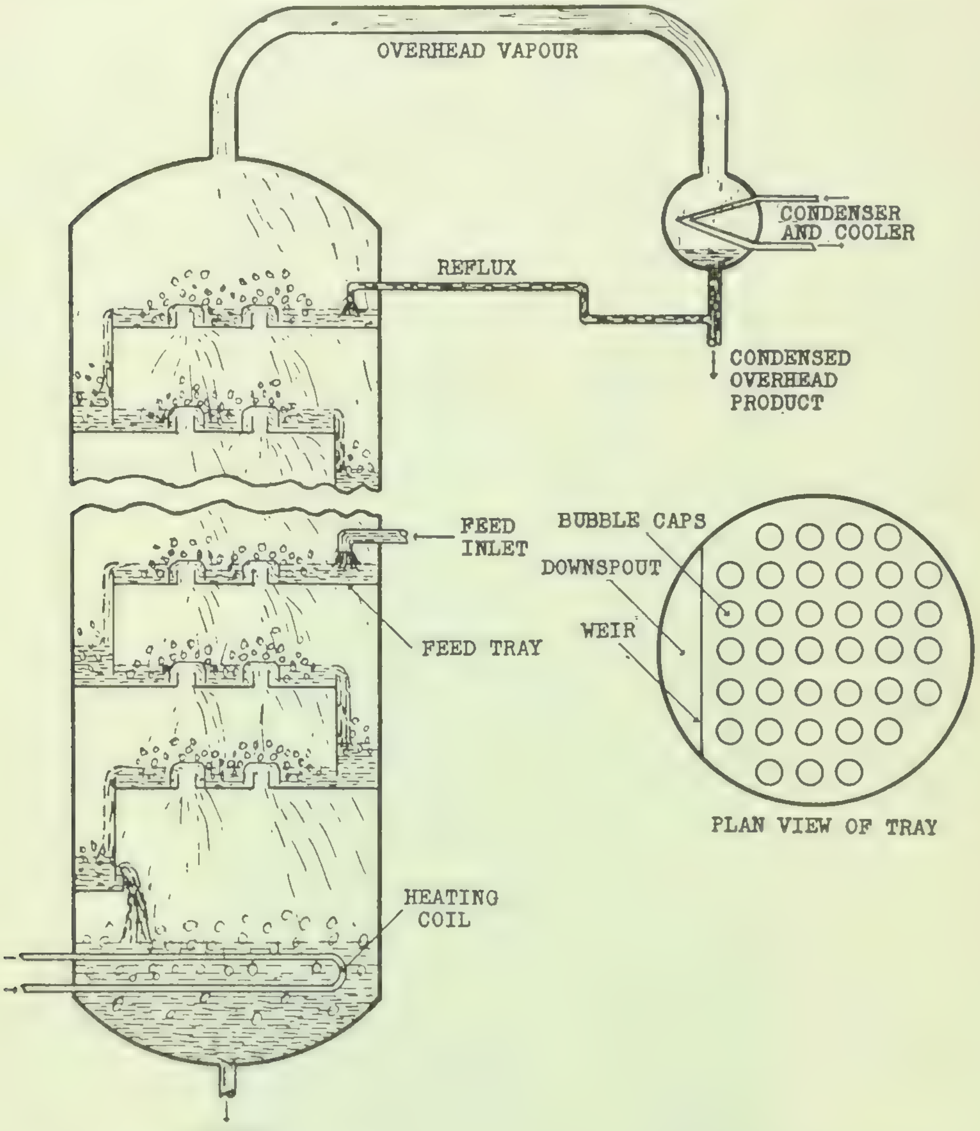


Fig. 184—A Diagram Showing the Inside of a Bubble Tower

Thus, the gas oils condense on the lower trays and kerosene on the cooler upper trays. Gasoline escapes out of the top of the tower as a vapour and is condensed outside the tower.

5. Treating Chemicals

In the previous section the separation of the crude petroleum into various fractions by distillation was considered. Most of these fractions must be treated with various chemicals to remove certain impurities. A few of the more important chemicals used for this purpose will now be considered briefly.

Gasolines, obtained from the fractional distillation process, are usually washed with concentrated *sulphuric acid.* The purpose of treating gasoline with sulphuric acid is to remove gum-forming substances, which are quite harmful to a motor. The gasoline is washed with *caustic soda* (NaOH) after the treatment with the acid. The sulphuric acid also attacks sulphur compounds, which are also very detrimental to a car motor.

A recent method of removing sulphur compounds consists of passing the hot vapours of the fraction under treatment through a porous bed of the mineral, bauxite. This material has the property of changing evil smelling sulphur compounds, such as the mercaptans, into hydrogen sulphide. The hydrogen sulphide is then removed by treating the fraction with lye (NaOH).

6. The Cracking Process

By 1910, the number of motor cars had so increased that oil men began to think about increasing the yield of gasoline obtained from crude oil. The average yield secured by ordinary distillation methods is about 20 per cent. It was necessary to discover some method of breaking down the heavier and less volatile hydrocarbons into lighter and more volatile products. A process, known as *cracking*, was developed by Burton, an American engineer, and its industrial application started about 1913. This invention has been responsible for a tremendous development of the petroleum industry since that date.

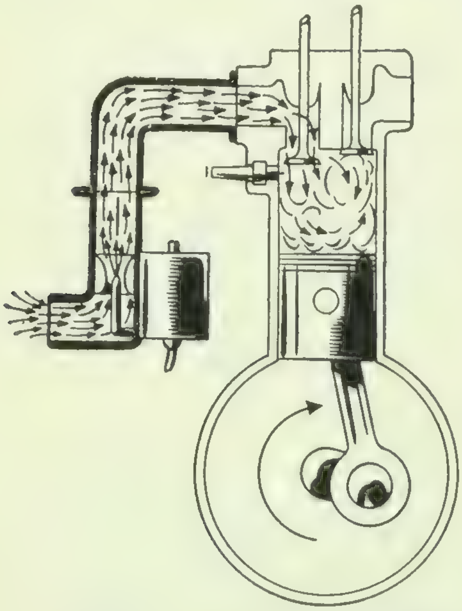
The decomposition of the heavier hydrocarbons can be done by heating the oil, under pressure, in specially constructed "cracking" stills. The products of this decomposition are lighter liquids and gases from which more gasoline is obtained by fractional distillation. Another method of cracking oil consists of passing the hot vapours, obtained by heating the oil, over a catalyst, such as aluminum chloride ($AlCl_3$). An advantage of this method is that it can be carried out at atmospheric pressure. A typical cracking reaction can be expressed by the following equation.

$$C_{12}H_{26} \longrightarrow C_6H_{14} + C_6H_{12}$$

Many of the compounds produced in the cracking process are very active chemically, and so they can be used to form many important materials, such as industrial alcohols, T.N.T., or synthetic rubber.

7. Anti-Knock Compounds

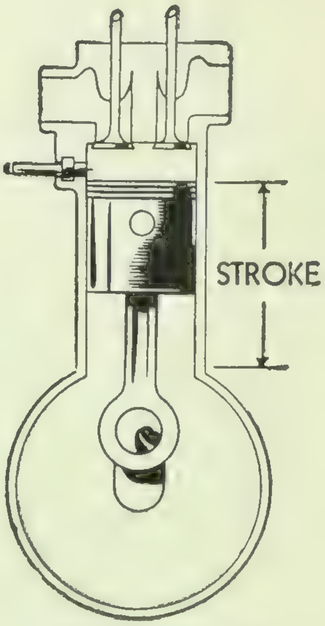
The power secured by the explosion of a mixture of air and gasoline vapour in the cylinders of an internal combustion motor, such as in the automobile (see Fig. 185), depends upon expansion taking place when the mixture explodes (see Fig. 186).



Courtesy of General Motors Products of Canada, Ltd

Fig. 185

The intake manifold distributes the mixture of combustible gasoline vapour and air to each cylinder during the intake stroke. Note how the fine spray of gasoline is introduced by the carburetor into the stream of air.

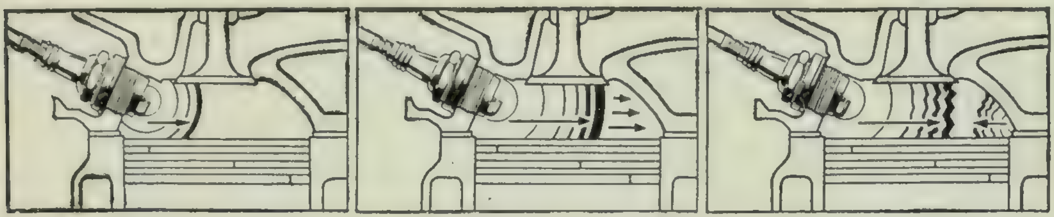


Courtesy of General Motors Products of Canada, Ltd.

Fig. 186

The Automobile Piston Power-Stroke

If, however, the gaseous mixture is forced into a smaller space before the explosion takes place, more power should be obtained. This principle is used in the high compression motors which are found in most modern automobiles. Such motors are said to have a certain compression ratio. For example, let us suppose that a motor has a compression ratio of four to one. This means that if a cylinder holds two pints with its piston down, the two pints are compressed into half a pint when the piston comes to the top of its stroke. The automobile piston power-stroke is shown in Fig. 186. With ordinary gasoline, these high compression motors, when in operation, give a pronounced "fuel knock." This means that there is a considerable loss of power when this type of engine fuel is used. The heat generated by the compression of the expanding gas, which is ignited by the spark plug, may be enough to produce an extremely rapid explosion of the remaining unburnt gas. This produces an immediate increase in pressure which causes the "fuel knock" already mentioned. In order to prevent knocking, the explosion must take place more or less like a wave, and it must give a slower "push" against the piston head. The best known anti-knock compound is a liquid, lead tetraethyl, Pb $(C_2H_5)_4$. This compound is made by the action of ethyl chloride on a lead-sodium alloy. The anti-knock fluid is a mixture of 3 parts by volume of lead tetraethyl, with 2 parts ethylene dibromide, $C_2H_4Br_2$. This mixture (about 3 c.c. per gallon of gasoline), along with a red dye, is added to the gasoline, and the gasoline treated in this way is known as "ethyl gas". During the combustion of this type of gasoline, lead oxide is formed. This substance is harmful to the cylinders, and so ethylene dibromide is added to change the lead oxide into the volatile lead bromide which escapes with the exhaust gases.



Courtesy of General Motors Products of Canada, Ltd.

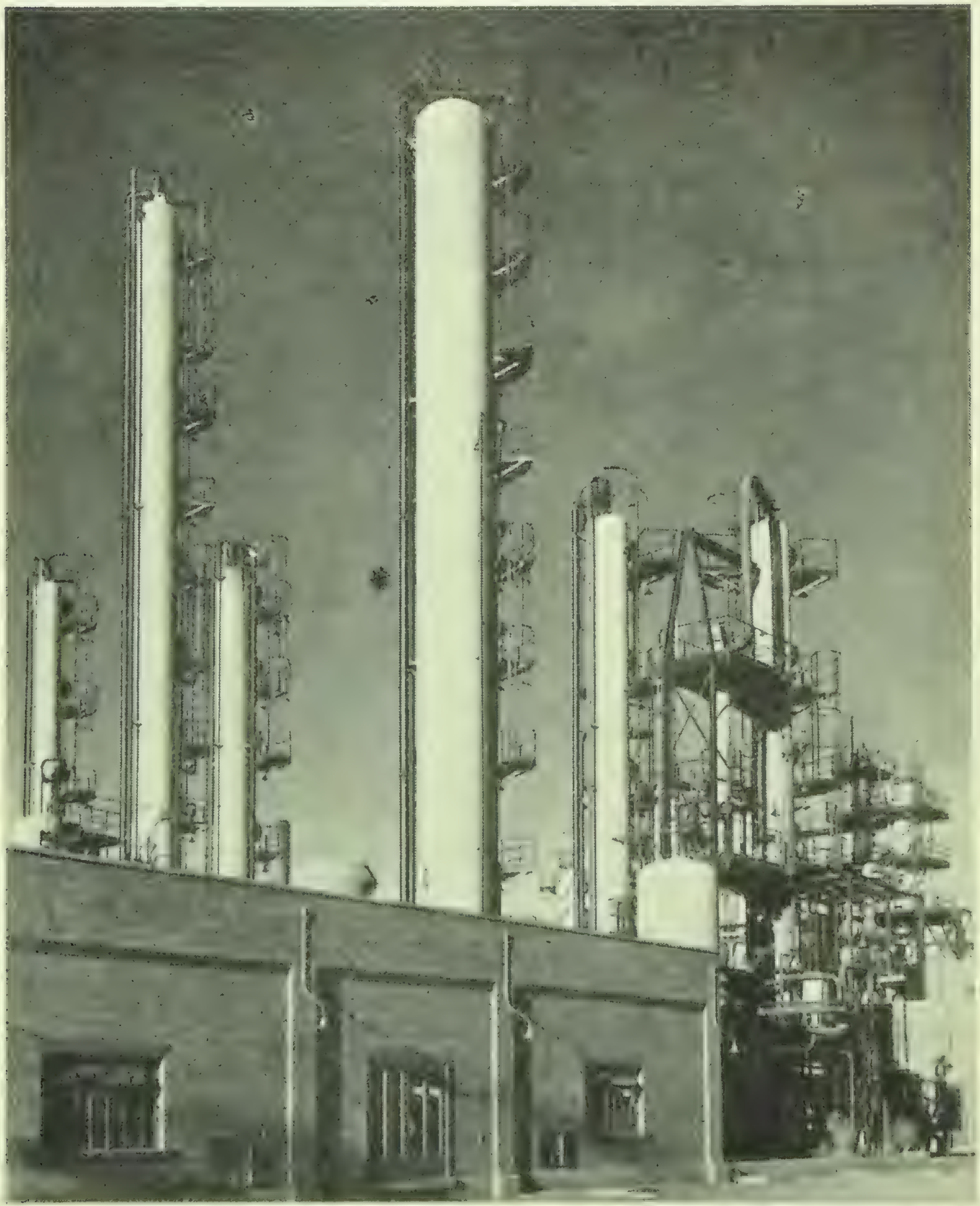
FIG. 187—THE CAUSE OF KNOCKING

(a) It takes about 1/250 of a second for the flame to travel across the combustion chamber. (b) The remaining unburnt gas is highly compressed and becomes very hot. (c) The unburnt gas explodes almost instantaneously and the two explosions meet. The total pressure on the piston head is raised in an instant by over a thousand pounds.

8. Octane Number

The octane number is the rating of a gasoline as to its anti-knock properties. It is determined by comparative tests in a specially designed engine, against standard fuels of known knock rating. The hydrocarbon, normal heptane, tends to knock, and it is given a knock rating of zero. On the other hand, *iso-octane*, which is the commercial name for 2,2,4-trimethyl pentane, possesses marked anti-knock properties, and it is given a knock rating of 100. The standard fuels are prepared by mixing heptane and iso-octane in various proportions. For example, a commercial gasoline has an octane number of 75 if on testing in a standard engine it knocks to the same extent as a mixture of 75 per cent iso-octane and 25 per cent normal heptane. Of course, gasoline with a high octane number knocks much less than one with a low rating. Gasolines with a rating of 75 or higher are needed for the efficient operation of the modern motor car.

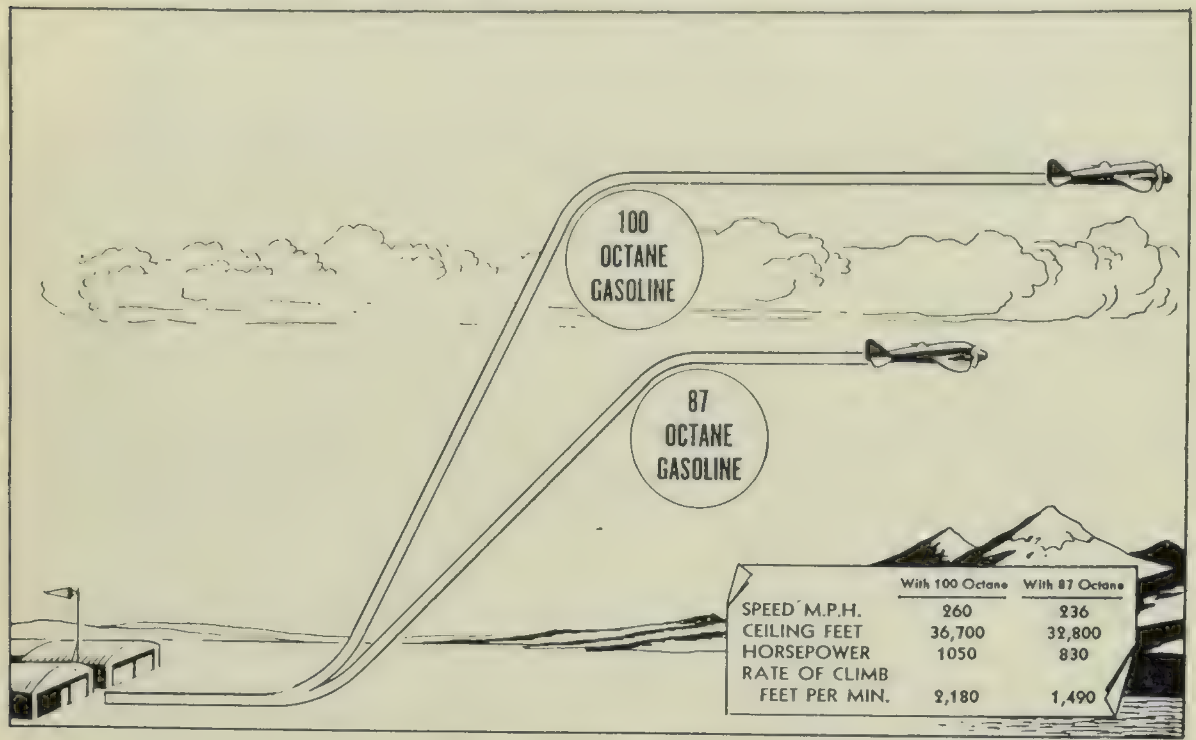
Research chemists have discovered how to make a hydrocarbon of the paraffin series combine with a hydrocarbon of the ethylene series in the presence of a catalyst. This type of re-



Courtesy of Imperial Oil, Limited

FIG. 188—AN ALKYLATION PLANT IN A LARGE MODERN CANADIAN OIL REFINERY. IT PRODUCES HIGH OCTANE ALKYLATE BLENDING AGENT FOR AVIATION GASOLINE

action is known by organic chemists as *alkylation* and modern refineries now have alkylation plants such as the one shown in Fig. 188. The hydrocarbons produced by this method are known as "alkylate." They have an octane rating of from 90 to 95, and are used in the production of aviation gasoline.



	With 100 Octane	With 87 Octane
SPEED M.P.H.	260	236
CEILING FEET	36,700	32,800
HORSEPOWER	1050	830
RATE OF CLIMB FEET PER MIN.	2,180	1,490

Courtesy of Imperial Oil, Limited

FIG. 189—DEMONSTRATION OF THE IMPORTANCE OF HIGH OCTANE RATING FOR AVIATION GASOLINE

Trials with a twin-engined light bomber have demonstrated the importance of high octane rating for aviation gasoline. The plane was operated with 87 octane aviation gasoline and then with 100 octane. The 100 octane fuel increased the top speed 24 miles per hour and the cruising speed 19 miles per hour. Rate of climb was increased from 1490 feet per minute to 2180. The time required to reach a height of 26,000 feet was decreased by seven minutes when 100 octane gasoline was used in the aircraft. The absolute ceiling was lifted from 32,800 feet to 36,700 feet.

The marked improvement in performance of the plane, when using 100 octane gasoline, was due to increased power. With 100 octane fuel the motor developed 1050 horsepower as compared to 830 when 87 octane gasoline was used. It has been reported that this fact contributed much to the victory of the Royal Air Force in the battle of Britain in September, 1940. The British planes used 100 octane fuel, whereas the German planes were fueled with 87 octane gasoline.

EXERCISES

1. (a) What is petroleum?
   (b) What is the meaning of the word petroleum and why is it a good description of this liquid?
2. (a) What country is the largest producer of crude oil?
   (b) Make a list of the chief oil producing countries.
   (c) Write a short note on Canada's petroleum resources.
3. Write a note on petroleum exploration.
4. (a) What is the purpose of the derrick in oil well drilling?
   (b) What are the two methods of drilling an oil well?
   (c) What is the essential difference between the two methods?
   (d) Write a note on drilling fluid.
5. (a) What is a gusher?
   (b) How is the crude oil stored at the wells?
   (c) Discuss briefly the transportation of petroleum from the wells to the refineries.
6. Write short notes on each of the following: fractional distillation of crude oil, a pipe still, a bubble tower, gasoline, gas oil.
7. Mention three chemicals used to treat gasoline and explain why they are used.
8. Write a note on the cracking process, making clear its importance in the petroleum industry.
9. (a) What is a high compression motor?
   (b) What is meant by fuel knock? Explain its cause.
   (c) How is fuel knock eliminated?
   (d) Why is ethylene dibromide used in ethyl gas?
10. (a) What is meant by the octane rating of a gasoline?
    (b) Discuss briefly how it is determined.
    (c) What is alkylate?
    (d) Why must aviation gasoline have a high octane rating? Explain briefly.

CHAPTER XLVII

GASEOUS FUELS

Gases are often used as fuels in the home and in industry instead of solid fuels. They have the following advantage over solid fuels.

(1) Elimination of smoke and ashes.
(2) Greater efficienty in burning.
(3) Easier temperature control.
(4) Ease of placing fuel in furnace.

Most industrial smoke consists of fine particles of unburnt coal suspended in the air. The elimination of this smoke results in a great saving of money. It has been calculated that the yearly loss of solid fuel as smoke in certain large industrial cities amounts to millions of dollars. It would appear then that the use of gaseous fuels is the most efficient and economical method of obtaining energy from our natural fuel resources. The chief gaseous fuels are coal gas, water gas, producer gas and natural gas. These will now be discussed briefly.

1. Coal Gas

In the chapter on carbon, it was found that coal gas is an important by-product in the production of coke from bituminous coal. A diagram of a coal gas plant is shown in Fig. 190. It shows that it consists of a retort, in which the coal is subjected

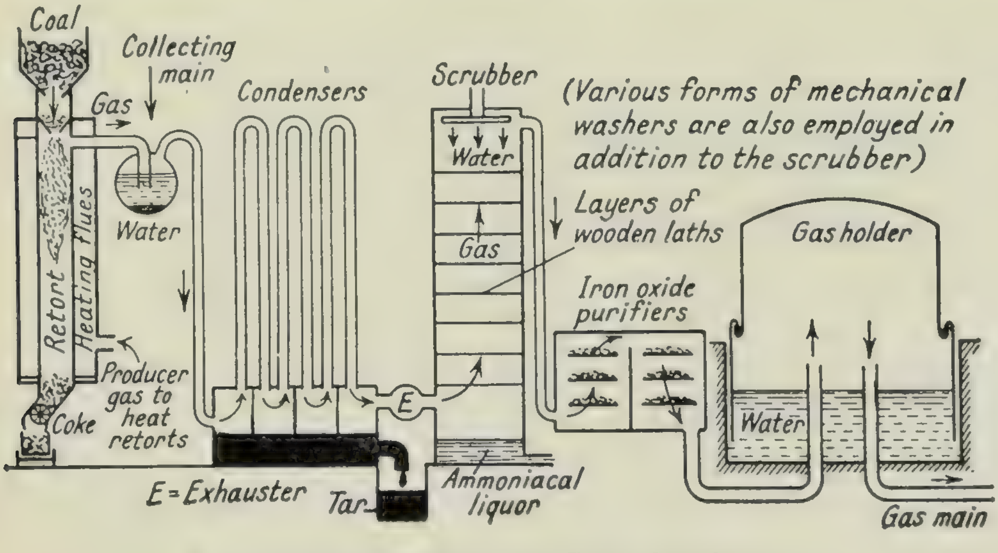


FIG. 190—DIAGRAM OF A COAL GAS PLANT

to destructive distillation; the collecting main; the scrubber; the iron oxide purifiers, which remove sulphur; and the gas holder. The gases, produced by the destructive distillation of the bituminous coal, escape from the retort and bubble through the water in the collecting main. In this part of the plant and in the condensers, the coal tar, water and other products, which are readily condensed and which are soluble, are removed from the gas. The gas then goes into the scrubber, which is a tall container filled with loose coke. Water is sprayed in at the top of the scrubber and, as it trickles down over the coke, it removes ammonia and some of the hydrogen sulphide from the gas. The rest of the hydrogen sulphide is eliminated from the gas in the iron oxide (Fe_2O_3) purifiers. The gas then passes into the gas holder for storage, and from there it goes under pressure into the city's gas mains.

The proportions of the components of coal gas depend upon the type of coal used and the temperature of the retort. The composition of a typical sample of the purified gas as delivered to consumers is shown in Table 24. The combustion of one cubic foot of such a coal gas would give about 500 British thermal units of heat.

TABLE 24—COMPOSITION OF COAL GAS

Component	Percentage
Hydrogen	53.0
Methane	28.5
Carbon Monoxide	9.3
Other Hydrocarbons (chiefly ethylene, acetylene and benzene)	3.8
Hydrogen Sulphide	nil
Carbon Dioxide	1.2
Nitrogen	3.8
Oxygen	0.4
	100.0

Many valuable by-products are obtained in the production of coal gas. The *ammonia* gas (NH_3) is usually allowed to react with dilute sulphuric acid to form ammonium sulphate, which is an important fertilizer. Of course, the *coal tar* yields many valuable materials which serve as starting points in the production of important dyes, drugs, explosives, plastics and other useful substances.

$$\text{1 ton of bituminous coal} \longrightarrow \begin{cases} \text{10,000 to 12,000 cu. ft. of gas} \\ \text{1300 to 1500 lb. of coke} \\ \text{15 to 30 lb. ammonium sulphate} \\ \text{10 to 12 gal. of coal tar} \end{cases}$$

2. Water Gas

This gas is produced when steam is passed through hot coal or coke. The steam is reduced by the carbon in the fuel according to the following equation.

$$H_2O + C \longrightarrow CO + H_2$$

The products of this reaction are carbon monoxide (CO) and hydrogen (H_2), and this mixture is known as *water gas.*

Combustion of this gas produces much less heat than coal gas, and so it is enriched by a process known as *carburetting.* A diagram of a carburetted water gas plant is shown in Fig. 191.

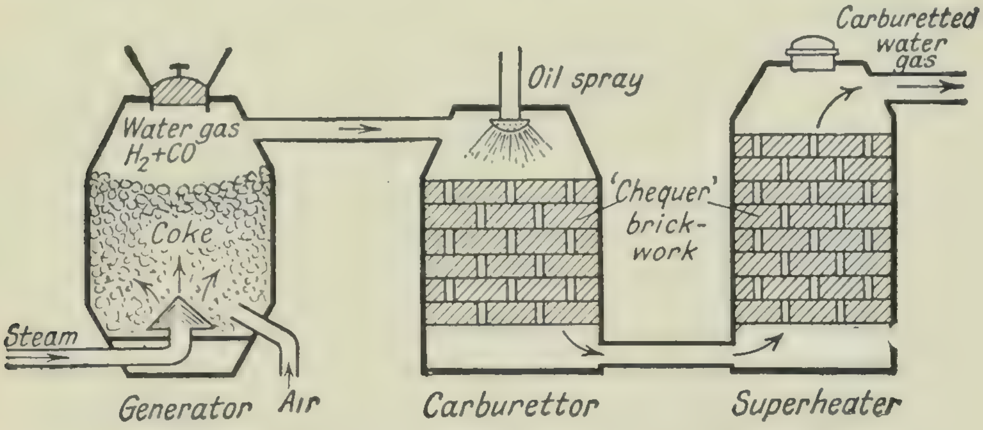


FIG. 191—CARBURETTED WATER GAS PLANT

Such a plant has a generator in which a high temperature (about 1400 C. (2552 F.)) is reached by the combustion of coke, which burns vigorously because of the blast of air forced in at the bottom of the apparatus.

$$C + O_2 \longrightarrow CO_2 + \text{heat}$$

This operation is known as the "blow." The next stage of the process consists of turning off the air and introducing steam. The steam reacts with the hot coke, producing about equal volumes of hydrogen and carbon monoxide. This reaction is endothermic (absorbs heat), and so it can only be carried out for a few minutes. This part of the process is known as the "run." Below 1000 C. the coke reacts with steam to produce carbon dioxide, which has no fuel value.

$$2\ H_2O + C \longrightarrow CO_2 + 2\ H_2$$

For this reason the steam is turned off before the low temperature is reached, and the generator is brought back to its normal high temperature, 1400 C., by an air blast. As shown in Fig. 191, the water gas goes from the generator to a carburettor and a superheater. These are towers containing chequered brickwork, and they have been heated beforehand by the waste gas of the "blow." As the water gas goes through these towers, petroleum oil is sprayed in at the top of the carburettor. As the oil passes through the superheater, it is decomposed (cracked) by the heat into gaseous unsaturated hydrocarbons.

The enriched water gas, known as *carburetted water gas*, is then purified by passage through scrubbers and condensers, and stored in a gas holder.

3. Producer Gas

This fuel gas is formed by blowing air through a deep bed of red-hot coke. This operation is carried out in a type of furnace called a "producer." A diagram of such a furnace is shown in Fig. 192. The equations for the reactions involved in this process are:

$$C + O_2 \longrightarrow CO_2$$
$$CO_2 + C \longrightarrow 2\ CO$$

The chief components of producer gas are carbon monoxide (about 30 per cent) and nitrogen (about 60 per cent). It also contains small amounts of carbon dioxide, hydrogen, methane and other hydrocarbons. Producer gas is used, as soon as it is manufactured, as a fuel in gas-burning industrial furnaces. It is also used to drive gas engines for power. It is interesting to know that blast furnace gas, formed as a by-product in the production of pig iron in the blast furnace, is almost the same as producer gas.

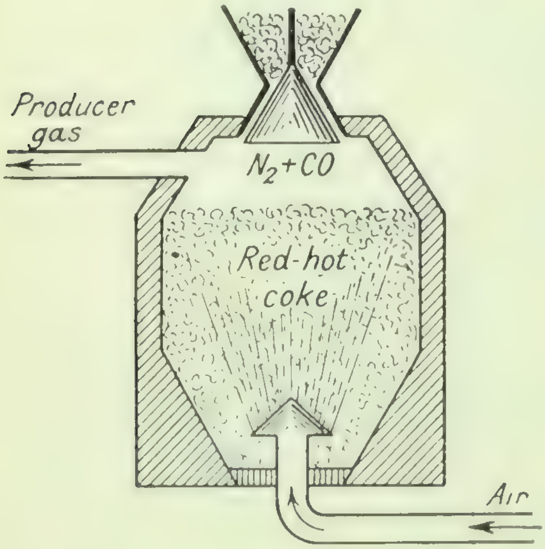


Fig. 192
A Producer Gas Furnace

4. Natural Gas

Natural gas is often found when drilling for oil and, in some cases, it occurs in formations which do not contain petroleum. The producing natural gas wells in Canada are in New Brunswick, Ontario, Saskatchewan, and Alberta. This important gaseous fuel consists chiefly of methane and hydrogen, along with certain of the higher hydrocarbons, such as propane and butane. Most samples of natural gas contain a very high proportion of methane, ranging from 50 to 95 per cent, depending upon the field from which it comes. Methane produces a great deal of heat when it burns, and this fact makes it a valuable fuel. The equation for its combustion is:

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O + \text{heat}$$

5. Flames

(1) Gas Flames. The ordinary combustion of most fuels is usually accompanied by a flame. The type of flame depends upon the material being burned. We are all familiar with the flames of burning wood, paper, coal, gas, and oil. However, we should remember that certain materials burn without the formation of a flame. For example, when charcoal burns, the solid gives off light, but no flame is produced. The flames observed during the burning of coal, oil, or a candle are due to the combustion of gases. These gases are produced from the combustible material by the heat given off during the burning of the fuel. In the case of solid fuels, such as coal, the gases are formed by the process of destructive distillation. In the case of liquid fuels, such as oil, the gases are formed by vaporization. Thus, *a flame can be defined as a region in which combustion of gases takes place, giving off heat and light.*

(2) The Structure of Flames. It can be shown by experiment that a flame consists of very hot gases, which sometimes contain very small *incandescent* (glowing) *solid particles.* It can also be shown by experiment that ordinary flames, such as those produced by a burning candle, kerosene lamp, or gas jet are "hollow." This is because the combustible gases can only undergo oxidation where they come in contact with the surrounding air. The inside of a flame, since it is not in contact with oxygen of the air, is made up of unburnt gases. This fact may be demonstrated by the following *experiments:*

(a) A clean piece of asbestos board is brought down on to a Bunsen flame for a few seconds. The result of this experiment is shown in Fig. 193 (a).

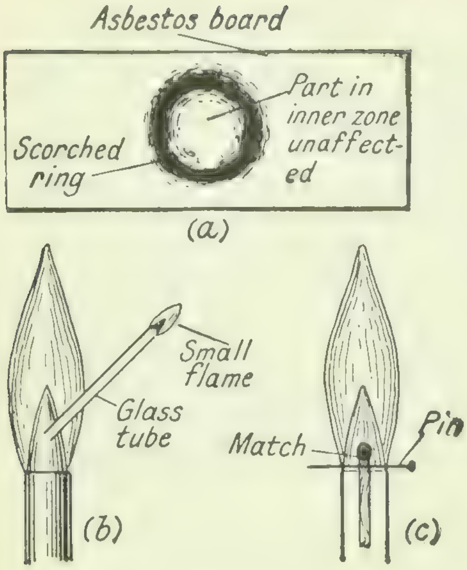


FIG. 193
THE INNER ZONE OF A FLAME

(b) The unburnt gases from the inner zone of a candle or of a Bunsen burner flame can be piped away by means of a short piece of glass tubing and burned at the end of the tube as shown in Fig. 193 (b).

(c) An ordinary match can be placed in a Bunsen burner as shown in Fig. 193 (c). It will stay unlit for some time after the gas has been ignited.

(3) THE ZONES OF A FLAME. Examination of candle, or luminous coal gas flames shows that they consist of four regions:

(1) Inner zone (unburnt gases).
(2) Luminous zone (light giving).
(3) Non-luminous mantle (hot outer zone).
(4) Blue zone (small and near base).

These regions are shown in Figs. 194 (a) and 194 (b). When the air intake of a Bunsen burner is properly adjusted, the luminous zone (2) will disappear and the non-luminous Bunsen flame consisting of three zones will be observed as shown in Fig. 194 (c).

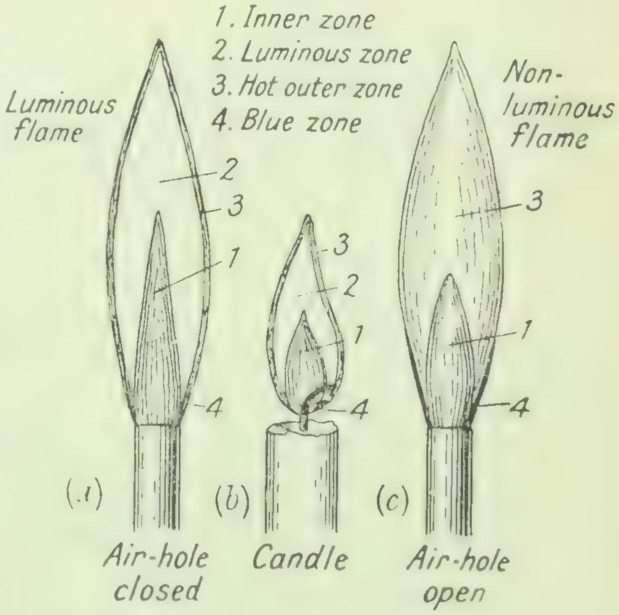


FIG. 194—THE ZONES OF FLAMES

(4) THE LUMINOSITY AND NON-LUMINOSITY OF FLAMES. An important cause of the luminosity of flames is the presence in them of minute incandescent (glowing) solid particles. Very small solid particles of the element carbon are formed in the luminous (light giving) zone of a candle or gas flame because of the incomplete combustion of the hydrocarbons in the gas. This is due to an insufficient supply of oxygen, and so these compounds

are decomposed by the heat of the flame to form small particles of free carbon. These particles become white-hot and give off light. When the gases come to the outer mantle, there is complete combustion because of the abundant supply of oxygen surrounding the flame.

The following *experiments* illustrate some of the ideas discussed above.

(a) Hold a clean porcelain evaporating dish over the luminous zone of a burning candle flame for several minutes. The presence of solid particles of carbon in this region will be indicated by the fact that the bottom of the dish will soon be covered with "soot."

(b) Sprinkle powdered charcoal or fine iron filings into a non-luminous Bunsen burner flame. The flame will become luminous due to the presence of the fine incandescent solid particles in it. The same effect will be observed when a "chalky" eraser, used to clean blackboards, is shaken over a non-luminous Bunsen burner flame.

When the air holes of a Bunsen burner are opened to allow plenty of air to become mixed with the gas, the flame is practically non-luminous. The best explanation of this effect appears to be that the incoming air *cools* and *dilutes* the reacting gases before they reach the flame. The cold incoming gases lower the temperature of the inner flame below that needed to decompose the hydrocarbons in the gas into free carbon. The dilution of the gas by an excess of air cuts down the speed with which the free carbon is formed. These two factors, therefore, tend to prevent the formation of the great excess of the very small solid particles of free carbon needed to furnish light, and so the flame is non-luminous.

6. Gas Burners

(1) THE BUNSEN BURNER. The construction of a Bunsen burner is shown in Fig. 195. As the gas comes up from the gas jet, it draws in air through the air-hole, and so a mixture of gas and air is admitted into the inside of the flame. This, as already explained, produces a non-luminous flame.

It is reported that the non-luminous Bunsen flame has a temperature of 1870° C. at its hottest part. The outer mantle of a Bunsen flame, in which there is an abundance of oxygen, is known as an *oxidizing flame.* On the other hand, the inner portion of the flame, in which there is an insufficient supply of oxygen and so combustion is not complete, is called a *reducing flame.* The outer mantle can bring about oxidation reactions because it has an excess of hot oxygen, obtained from the air. The inner flame, however, can bring about reduction reactions since it has an excess of hot coal gas which contains an appreciable amount of hydrogen. It is the hot hydrogen which serves as the reducing agent.

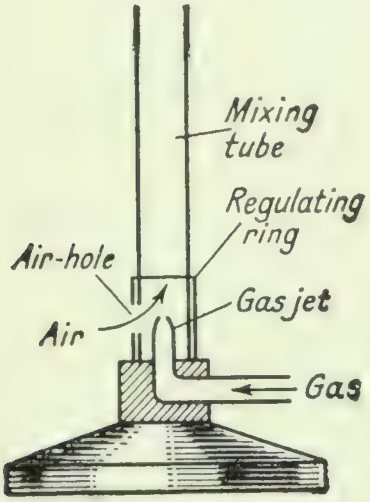


Fig. 195
The Bunsen Burner

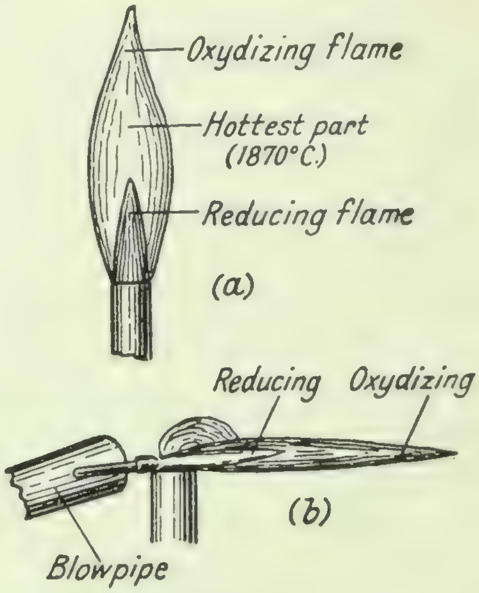


Fig. 196
Oxidizing and Reducing Flames

(2) Domestic Burners. These burners are used in gas stoves and other types of domestic heaters. They are constructed on the same principle as that of the Bunsen burner. However, they have numerous small openings, which produce many little flames in a row or ring in place of one large flame (see Fig. 197).

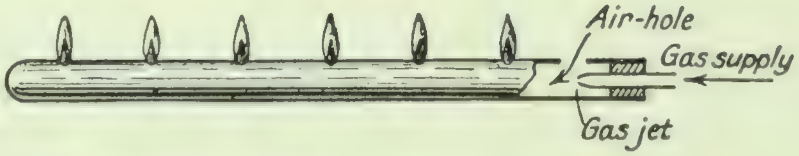


Fig. 197—A Domestic Gas Burner

(3) The Incandescent Gas Burner. This burner, sometimes known as the Welsbach gas lamp, is also based on the same idea as the Bunsen burner. It contains a mantle, made from thorium dioxide, ThO_2, (99 per cent) and cerium dioxide, CeO_2, (1 per cent), which glows very brightly when heated (see

Fig. 198), producing about ten times as much light as does an ordinary burner using the same amount of gas.

(4) Blowpipes. A diagram of a simple blowpipe is shown in Fig. 29, page 52. This shows that the construction of a blowpipe is based upon the same principle as that of a Bunsen burner. However, in a blowpipe air or oxygen is forced under pressure into the inside of the flame rather than sucked in by the gas coming out from the jet. The combustible gas, such as hydrogen, is forced through the outer tube and ignited at the tip. The oxy-hydrogen blowpipe, invented in 1801, was the first to be used commercially. It has been replaced to a very large extent by more efficient blowpipes, although it is still employed for certain tasks, such as the manufacture of quartz containers. The oxy-acetylene blowpipe is used extensively in industry for welding and cutting steel and other alloys.

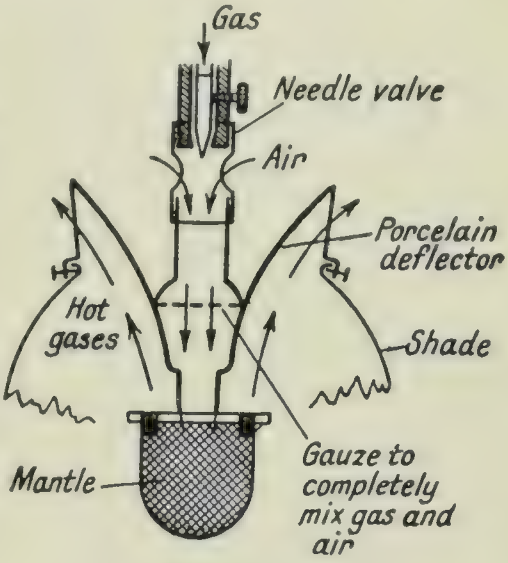


Fig. 198
An Incandescent Gas Burner

EXERCISES

1. (a) What are some of the advantages of fuel gases?
   (b) Tabulate the chief industrial gases.
   (c) Discuss carefully any two of the gases listed in (b).
2. (a) What is a gas flame?
   (b) Write a short note on the structure of flames.
   (c) Tabulate the zones of a flame.
3. (a) What is the cause of the luminosity of a flame?
   (b) How can a luminous Bunsen flame be made non-luminous?
   (c) What is the best explanation of the non-luminosity of flames?
4. What is the difference between an oxidizing and a reducing flame?
5. Tabulate the chief types of gas burners. In what way are they all similar?

Chapter XLVIII

THE ALCOHOLS AND ETHERS

1. Derivatives of the Hydrocarbons

The hydrogen atoms in the molecules of hydrocarbons can be replaced or substituted by other atoms or groups. Compounds formed in this way are known as *derivatives* of the hydrocarbons. For example, one atom of hydrogen (H) in the methane (CH_4) molecule can be replaced by a hydroxyl radical (OH) to form a molecule of methyl alcohol (CH_3OH). That part of the hydrocarbon molecule which remains unchanged in the derivative is known as an *alkyl* radical. Thus, the CH_3— part of methyl alcohol, called the methyl radical, is an example of an alkyl radical. These radicals cannot exist in the free state and they all have a valence of one. Table 25 contains the names and formulas for the alkyl radicals which correspond to the first ten members of the methane or paraffin series of the hydrocarbons.

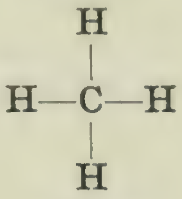
Table 25—Alkyl Radicals

Formula	Name	Formula	Name
CH_3	Methyl	C_6H_{13}	Hexyl
C_2H_5	Ethyl	C_7H_{15}	Heptyl
C_3H_7	Propyl	C_8H_{17}	Octyl
C_4H_9	Butyl	C_9H_{19}	Nonyl
C_5H_{11}	Amyl	$C_{10}H_{21}$	Decyl

In addition to the derivatives of the methane hydrocarbon series, we have of course, derivatives of the ethylene, acetylene and benzene series. These are studied in detail in courses dealing with organic chemistry. In this text, however, we shall only be able to consider a few of the more important derivatives of the methane hydrocarbons.

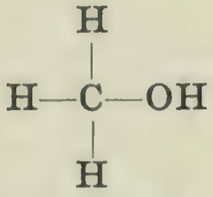
2. The Alcohols

The alcohols are compounds formed by replacing one or more hydrogen atoms in a hydrocarbon by the corresponding number of hydroxyl groups (OH). The structural formulas for several methane hydrocarbons and the alcohols derived from them are given below.



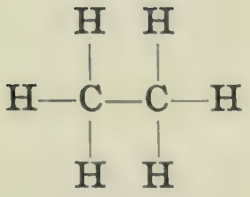
$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H-C-H} \\ | \\ \mathrm{H} \end{array}$$

(methane)



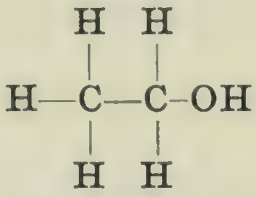
$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H-C-OH} \\ | \\ \mathrm{H} \end{array}$$

(methyl alcohol)



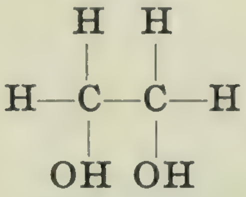
$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

(ethane)



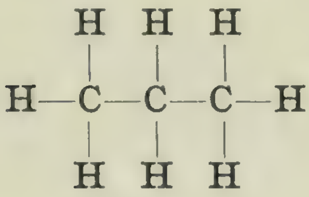
$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{OH} \\ & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

(ethyl alcohol)



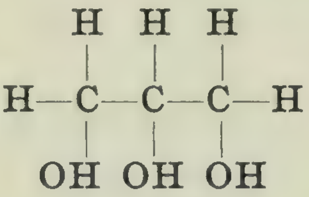
$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & \\ & & \mathrm{OH} & & \mathrm{OH} & & \end{array}$$

(ethylene glycol)



$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

(propane)



$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & | & & \\ & & \mathrm{OH} & & \mathrm{OH} & & \mathrm{OH} & & \end{array}$$

(glycerine)

Methyl alcohol and ethyl alcohol are known as *monohydric* alcohols because they only contain one hydroxyl group per molecule. Ethylene glycol, however, is called a *dihydric* alcohol since it has two hydroxyl radicals in its molecule. Glycerine, having three OH groups in its molecule, is known as a *trihydric* alcohol.

The usual method of naming an alcohol is to use the name of the alkyl radical which it contains along with the word alcohol. For example, C_2H_5OH is called ethyl alcohol. In 1892 a group of organic chemists met at Geneva, Switzerland, where they drew up an international system of naming organic compounds.

TABLE 26—A FEW TYPICAL ALCOHOLS

Formula	Ordinary Name	Geneva Name
CH_3OH	Methyl alcohol	Methanol
C_2H_5OH	Ethyl alcohol	Ethanol
C_3H_7OH	Propyl alcohol	Propanol
C_4H_9OH	Butyl alcohol	Butanol
$C_5H_{11}OH$	Amyl alcohol	Pentanol
$C_6H_{13}OH$	Hexyl alcohol	Hexanol
$C_2H_4(OH)_2$	Ethylene glycol	Ethanediol —1, 2
$C_3H_5(OH)_3$	Glycerine	Propanetriol —1, 2, 3

This is known as the Geneva system and it is used by nearly all organic chemists throughout the world. Alcohols derived from the methane hydrocarbons are named, according to this system, by replacing the ending *e* of the hydrocarbon by the ending *ol*. Thus, the alcohol derived from ethane is called ethan*ol*. The formulas and names, according to both methods, of a few typical alcohols are given in Table 26.

Since methyl alcohol, ethyl alcohol and glycerine are quite important commercially, they will now be considered in some detail.

3. Methyl Alcohol (Methanol), CH_3OH.

This alcohol is also known as wood alcohol, because until recent times it was produced by the destructive distillation of wood. Hard woods, such as birch and beech, appear to be the best for this purpose. This method of securing wood alcohol is very wasteful, only about two gallons of the alcohol being obtained from a ton of wood. Of course, acetic acid and acetone are also produced along with the methyl alcohol. The modern method consists of passing water gas, a mixture of hydrogen and carbon monoxide, under pressure (200 atmospheres) over a suitable catalyst (zinc oxide) at a temperature of about 400° C.

$$2\ H_2 + CO \longrightarrow CH_3OH$$

This process of producing methyl alcohol is known as *hydrogenation* of carbon monoxide. It is considerably cheaper than the destructive distillation of wood and gives almost pure methanol.

Methyl alcohol is a colourless liquid which has a boiling point of about 66° C. It is a very poisonous substance, often causing death if taken internally. The vapour from this alcohol produces blindness as it destroys the optic nerve. Some of the pioneer organic chemists lost their eyesight when doing research work with this alcohol. Wood alcohol burns in air, and so it can be used as a source of heat.

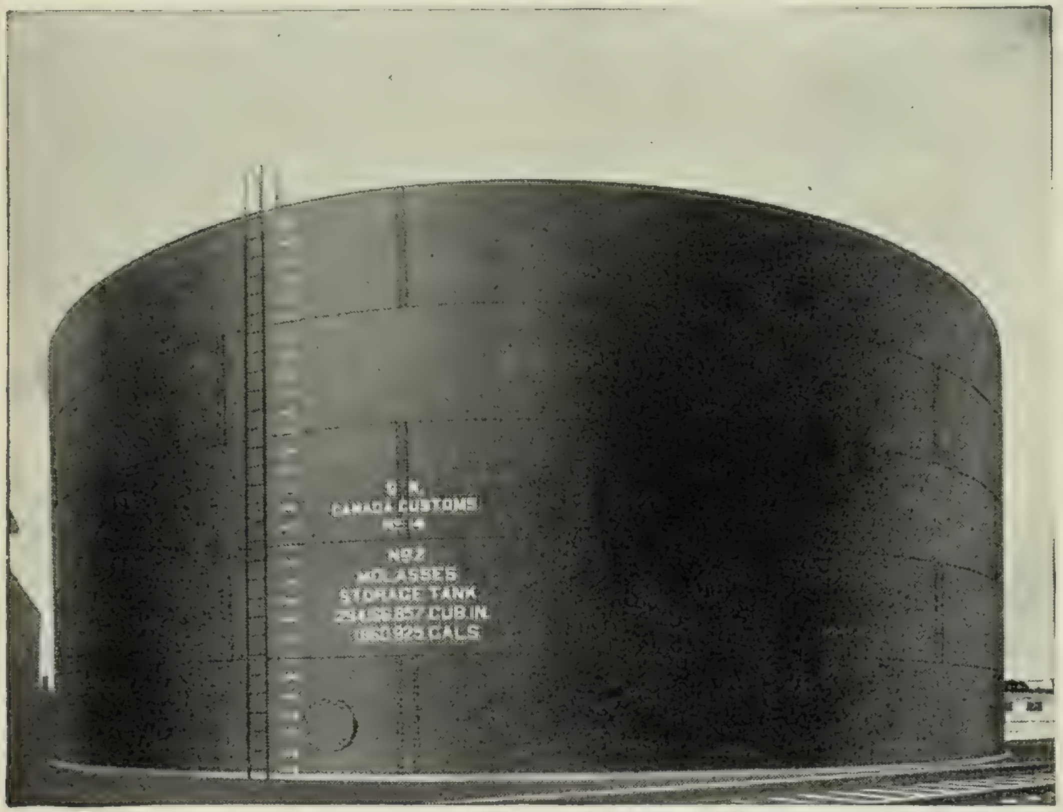
$$2\ CH_3OH + 3\ O_2 \longrightarrow 2\ CO_2\uparrow + 4\ H_2O$$

Methanol is a good solvent for shellacs and resins.

Wood alcohol has a number of important industrial uses. Because of its property of dissolving shellacs and resins, it is used considerably in the manufacture of varnishes and shellacs. It is also used in large quantities in the manufacture of formaldehyde (formalin), dyes, and drugs. Certain substances are added to pure ethyl alcohol to make it unfit for internal consumption. These substances are known as denaturants and methyl alcohol is often used for this purpose. For example, the ethyl alcohol used in hospitals is denatured by mixing ten gallons of wood alcohol with 90 gallons of pure ethyl alcohol.

4. Ethyl Alcohol (Ethanol), C_2H_5OH

This alcohol is the most common and important of all alcohols. It is sometimes known in commerce as grain alcohol or simply as "alcohol." Ethyl alcohol has been prepared from earliest times by *fermentation*. The two chief industrial methods of producing ethyl alcohol are the fermentation of molasses and the fermentation of grains or vegetables which are rich in starch. These two methods will now be considered briefly.



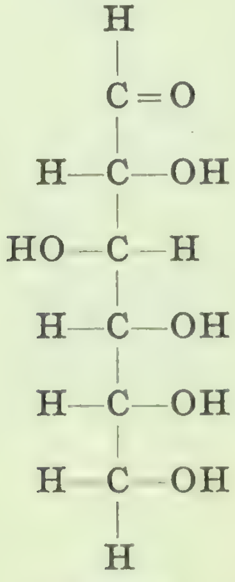
Courtesy of Gooderham and Worts, Ltd.

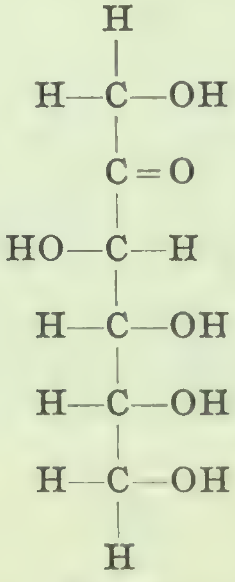
FIG. 199—THIS TANK CONTAINS MORE THAN ONE MILLION GALLONS OF MOLASSES, WHICH ARE USED TO MAKE INDUSTRIAL ALCOHOL

The fermentation of molasses requires yeast, which is a low order of plant life. The yeast cells, in their growth, produce some remarkable substances known as *enzymes*. These are nonliving, complex organic materials, found in plants and animals, which act as catalysts for certain reactions. Two enzymes, zymase and invertase (sucrase) are present in yeast, and they serve as catalysts in changing the cane sugar in the molasses into ethyl alcohol and other products. Under the influence of the invertase, the sucrose ($C_{12}H_{22}O_{11}$) molecules in the molasses of cane sugar or beet sugar are broken down by hydrolysis into two simpler sugars, glucose and fructose. The equation for this reaction is:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{invertase}} \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}$$

This mixture of glucose and fructose is known as *invert sugar*, and the process is called the inversion of cane sugar. It is observed from the above equation that glucose and fructose have the same molecular formula and such compounds are known as *isomers*. This phenomenon which is often encountered in organic chemistry is called *isomerism*. *Isomers are compounds which have the same molecular formula, but they possess different physical and chemical properties.* Their differences in properties are due to the fact that isomers have different structural formulas. To illustrate this fact the structural formulas for glucose and fructose are shown below.


(glucose)


(fructose)

Yeast contains another enzyme, zymase, which serves as a catalyst to convert the molecules of glucose and fructose into ethyl alcohol and carbon dioxide according to the following equation.

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2\ C_2H_5OH + 2\ CO_2\uparrow$$

It requires about 50 to 60 hours for the fermentation process to be complete. The carbon dioxide is collected and purified.

It is used to make dry ice or it may be compressed into cylinders for use in industry. Alcohol produced in this way contains water and other impurities, which are removed by fractional distillation. The final product consists of about 95 per cent pure alcohol, the other five per cent being chiefly water. For most industrial purposes, alcohol of this concentration or more dilute is used, and so alcohol is usually stored as 95 per cent.

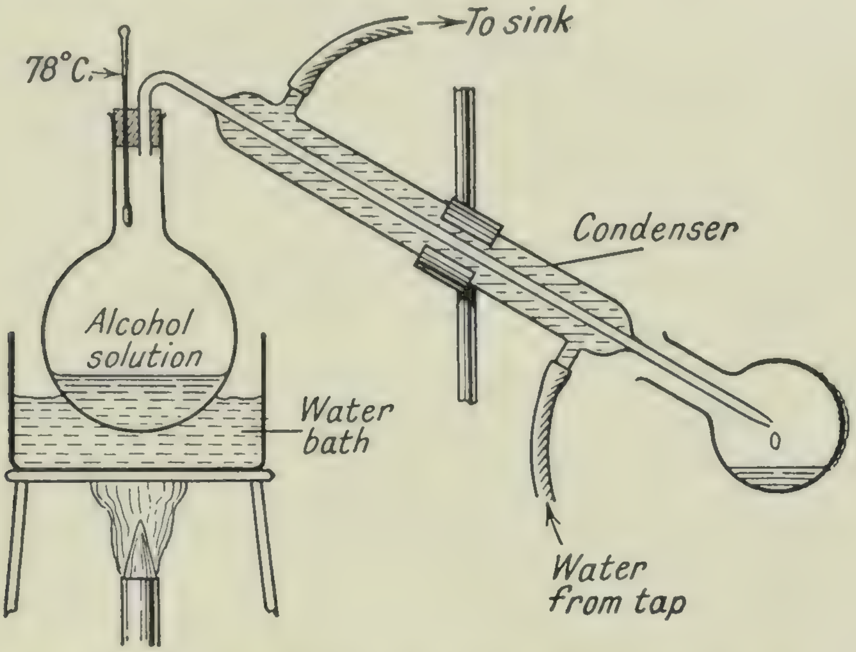


FIG. 200—THE LABORATORY DISTILLATION OF ALCOHOL

Starch, in the form of grain, has been used for the production of alcohol from earliest times. Vegetables, rich in starch, are also used for this purpose. The starch cannot be directly fermented by yeast, and so it must be first converted into sugar. This is brought about by *diastase*, an enzyme found in malt (sprouted barley). The diastase hydrolyzes the starch into malt sugar, known as maltose, and dextrin, a gum. The equation for this reaction is:

$$\underset{\text{(starch)}}{3\ C_6H_{10}O_5} + H_2O \xrightarrow{\text{diastase}} \underset{\text{(maltose)}}{C_{12}H_{22}O_{11}} + \underset{\text{(dextrin)}}{C_6H_{10}O_5}$$

When this change has taken place, yeast is added. The enzyme, invertase, in the yeast converts the maltose into glucose. Under the influence of the enzyme, zymase, the glucose is changed into ethyl alcohol and carbon dioxide.

Ethyl alcohol is a colourless liquid which has a characteristic odour and a sharp burning taste. The boiling point of pure ethyl alcohol is 78.4° C. It dissolves in water in all proportions. This substance burns to produce carbon dioxide and water.

$$C_2H_5OH + 3\ O_2 \longrightarrow 2\ CO_2 + 3\ H_2O$$

Alcohol has a number of important uses. Perhaps the largest single use of alcohol in Canada is for the protection of automobile radiators from freezing. Over one million gallons of this liquid are used every year for this purpose. The very low freezing temperature of ethyl alcohol (—114°C.) along with a medium boiling point makes it a good anti-freeze. As a solvent, alcohol is next to water in importance. There are many chemical processes in which alcohol is essential. Almost every article used in the home involves the use of alcohol at some stage of its manufacture.

Alcohol is used in the manufacture of varnishes, lacquers, rayon, paints, bakelite, food products, artificial leather, dyes, moving picture films, linoleum, drugs, cosmetics, ether, electrical goods and many other products. Alcohol is one of the chief substances upon which the entire organic chemical industry is based.

Alcohol is an important material in time of war. When gasoline is mixed with absolute alcohol, a fuel with a high octane rating is obtained for aircraft. T.N.T., cordite, smokeless powder, and other high explosives require ethyl alcohol in their production. The preparation of fulminate compounds, used in percussion caps, requires alcohol.

5. Glycerine (propanetriol—1, 2, 3), $C_3H_5(OH)_3$

This alcohol is also known as *glycerol.* It is produced as a by-product in the manufacture of soap.

$$\text{Fat} + \text{Lye} \longrightarrow \text{Soap} + \text{Glycerine}$$

Glycerine is a colourless, odourless, syrupy liquid. It has a sweet taste and absorbs moisture from the air. This liquid is soluble in water and alcohol in all proportions.

The most important use of glycerine is to make *nitroglycerine.* This compound is produced when glycerine is added to a mixture of concentrated nitric and sulphuric acids, the temperature being carefully regulated to prevent an explosion. The equation for this reaction is:

$$C_3H_5(OH)_3 + 3\ HNO_3 \longrightarrow \underset{\text{(nitro-glycerine or glyceryl trinitrate)}}{C_3H_5(NO_3)_3} + 3\ H_2O$$

The concentrated sulphuric acid is used to remove the water which is formed. When nitro-glycerine explodes, a number of gaseous substances are formed. These include CO_2, H_2O, N_2, O_2 and NO, and the heat of the reaction (4250°C.) causes these gases to expand rapidly to many times their original volume. The complete combustion and explosion of one kilogram of nitro-glycerine produces 715 litres of gas at S.T.P. It is this terrific expansion which gives such power to the explosion.

Explosive chemists give the following equation for the explosion of nitro-glycerine.

$$32\ C_3H_5(NO_3)_3 \longrightarrow 96\ CO_2 + 80\ H_2O + 6\ NO + 45\ N_2 + 5\ O_2$$

Nitro-glycerine is a very dangerous liquid to handle and explodes quite readily. However, in 1867, Alfred Nobel, a Swedish engineer discovered *dynamite* when he mixed nitro-glycerine with an inert substance, such as infusorial earth, known as "kieselguhr." Dynamite can be handled with much less risk than liquid nitro-glycerine and none of its explosive properties are lost. At the present time, sawdust, starch, and wood pulp are used instead of kieselguhr, and oxidizing agents

Courtesy of Canadian Industries, Ltd.

FIG. 201—A BLAST INVOLVING SEVERAL THOUSAND POUNDS OF DYNAMITE BLOWS UP A COFFERDAM DURING CONSTRUCTION OF A LARGE QUEBEC HYDRO-ELECTRIC POWER PLANT

such as sodium or ammonium nitrate are added to assist the combustion of the inert material. For example, an ordinary commercial dynamite would have the following composition approximately: 30 per cent nitro-glycerine, 15 per cent sawdust, and 55 per cent ammonium nitrate. Nitro-glycerine is very well suited to blasting operations due to its great shattering force. It is used in clearing land of stumps, in quarrying rock, mining coal, and in engineering projects, such as the making of railroad tunnels through mountains.

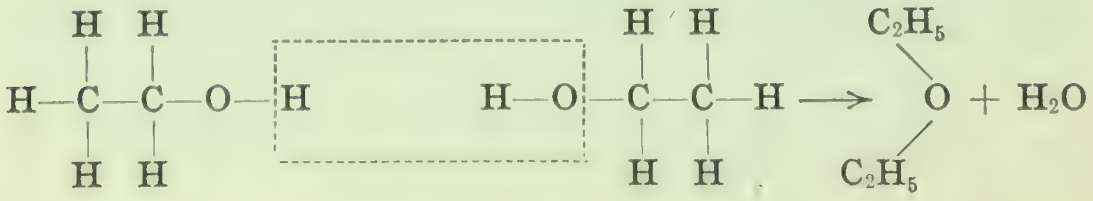
Glycerine has many other uses in commerce. It is used to prevent the drying out of various products, such as ink, cigarettes and smoking tobacco. It is used in medicine and as a sweetening agent in the manufacture of confections. Glycerine is used to a considerable extent in the manufacture of hand lotions, such as glycerine and rose water, soaps, cosmetics, and perfumes. It is sometimes used as an anti-freeze. It is also used in making the ink for rubber stamps.

6. The Ethers

Ethers may be considered as being organic compounds derived from water, HOH, by replacing both hydrogen atoms with alkyl radicals. Thus, *R-O-R* can be written as a general formula for the ethers, where the R stands for an alkyl radical. The R's may be the same or different. $C_2H_5—O—C_2H_5$ for example, is the formula for diethyl ether, usually known as "ether." Of course, the ethers are really organic oxides and could be represented by the formula R_2O. Thus, diethyl ether could be called ethyl oxide and its formula could be written as $(C_2H_5)_2O$.

Diethyl ether, $C_2H_5—O—C_2H_5$ (also called *ether*, sulphuric ether, ethyl ether and ethyl oxide), is the most important member of the ether family of organic compounds.

Ether is prepared by heating a mixture of ethyl alcohol and concentrated sulphuric acid at about 150° C. The sulphuric acid, because it is a powerful dehydrating agent, removes one molecule of water from two molecules of the alcohol according to the following equation:



Ether is a colourless liquid which has a very characteristic odour. It is a very volatile liquid, boiling at 35° C., and its vapour is very inflammable, burning with a luminous flame. Ether is an excellent solvent for fats, oils, resins, waxes and gums.

Ether is, perhaps, best known for its use as an anesthetic in surgery. It is also used as a solvent for many organic materials, especially fats, waxes and oils. Ether is used along with alcohol in the production of guncotton.

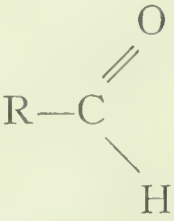
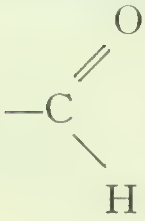
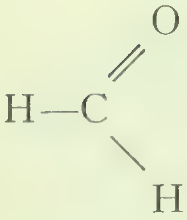
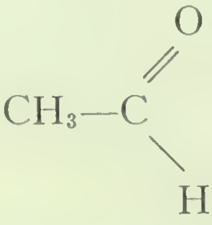
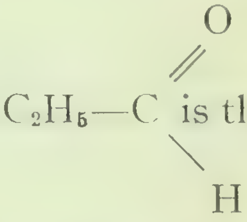
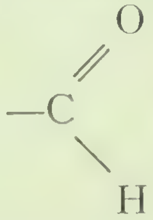
EXERCISES

1. (a) Why is methyl alcohol considered to be a derivative of methane?
   (b) What is an alkyl radical? Give the formulas and names for five alkyl radicals.
2. (a) What is an alcohol?
   (b) Discuss one commercial method of preparing methyl alcohol.
   (c) Tabulate the chief properties of wood alcohol.
   (d) Give three uses of methyl alcohol.
3. (a) Discuss the preparation of ethyl alcohol from molasses.
   (b) Write a note on the production of ethyl alcohol from grains or vegetables.
   (c) Tabulate the chief properties of ethyl alcohol.
   (d) Make a list of five uses of ethyl alcohol.
   (e) What are isomers? Illustrate your answer with two structural formulas.
4. Discuss glycerine under the headings: (1) preparation, (2) properties, (3) uses.
5. (a) What is an ether?
   (b) Write the equation for the preparation of diethyl ether.
   (c) What are the chief properties and uses of ether?

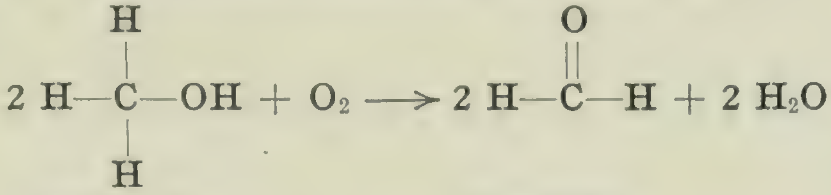
CHAPTER XLIX

ALDEHYDES, KETONES, ORGANIC ACIDS, ESTERS, FATS AND OILS, AND SOAPS

1. Aldehydes

The general formula for aldehydes is  $\mathrm{R{-}C}\begin{matrix} /\!\!/\mathrm{O} \\ \diagdown\mathrm{H}\end{matrix}$. R stands for an atom of hydrogen, or in most cases, an alkyl radical, and  $\mathrm{{-}C}\begin{matrix} /\!\!/\mathrm{O} \\ \diagdown\mathrm{H}\end{matrix}$ is known as the *aldehyde radical.* For example,  $\mathrm{H{-}C}\begin{matrix} /\!\!/\mathrm{O} \\ \diagdown\mathrm{H}\end{matrix}$ is the formula for formaldehyde, and in this case the R is a hydrogen atom.  $\mathrm{CH_3{-}C}\begin{matrix} /\!\!/\mathrm{O} \\ \diagdown\mathrm{H}\end{matrix}$ is the formula for acetaldehyde and here the R is the methyl radical. Again,  $\mathrm{C_2H_5{-}C}\begin{matrix} /\!\!/\mathrm{O} \\ \diagdown\mathrm{H}\end{matrix}$ is the formula for propionaldehyde, in which the R is the ethyl radical, C_2H_5. Thus, with the exception of formaldehyde, we may think of the aldehydes as being formed by replacing a hydrogen atom of a hydrocarbon by the  $\mathrm{{-}C}\begin{matrix} /\!\!/\mathrm{O} \\ \diagdown\mathrm{H}\end{matrix}$ group.

Formaldehyde is of importance in industry, and so it will be considered briefly. It is prepared by the oxidation of methyl alcohol by air. The reaction requires a catalyst, copper or silver, and the temperature needed is about 300° C.



$$2\ \mathrm{H}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}-\mathrm{OH} + \mathrm{O_2} \longrightarrow 2\ \mathrm{H}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{H} + 2\ \mathrm{H_2O}$$

(methyl alcohol) (formaldehyde)

Formaldehyde is a colourless gas which is extremely soluble in water. This gas has a pungent, penetrating odour, and is a powerful disinfectant.

Formaldehyde is available in commerce as a 40 per cent solution under the name of *formalin.* This solution serves as a disinfectant and as a preservative of specimens, such as frogs, in biology laboratories. It is used to a considerable extent in the preparation of certain dyes. Grains and potatoes are also disinfected, before being used as seed, by means of formalin.

Large quantities of formaldehyde are used in the production of synthetic *resins* or *plastics.* For example, "bakelite," discovered by Dr. Leo. H. Baekeland in 1909, is made by heating a mixture of *phenol* (obtained from coal-tar) and formaldehyde under pressure and in the presence of a catalyst. The introduction of this material marked the beginning of the modern plastic industry. Many changes were made in the original formula, resulting in resin-like materials with special properties. Today hundreds of products are sold under the trade name "bakelite." For example, it is used in the manufacture of fountain pens, phonograph records, pipe stems, and as an insulator in electrical devices, such as rheostats, push-buttons, telephone receivers and transmitters, and many accessories for automobiles. Formaldehyde is also used in the production of plastics from the following substances: casein (curds of milk), gelatin, albumen, and urea.

2. Ketones

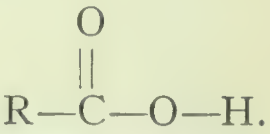
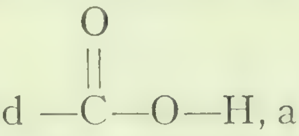
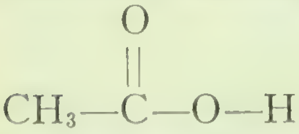
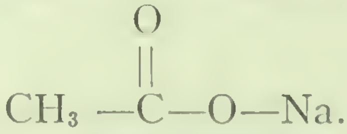
The general formula for ketones is $\mathrm{R}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R}$. The R usually stands for an alkyl group, and the $-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-$ is known as the *carbonyl* group. *Acetone*, $\mathrm{CH_3}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{CH_3}$, is the most important ketone, and so it will be considered briefly.

Acetone was until quite recently obtained by the destructive distillation of wood. It will be recalled that the four chief products obtained in that process are charcoal, methyl alcohol, acetic acid and acetone. Acetone is now prepared, for the most part, by a special fermentation method from corn starch. It is also obtained as a by-product of the petroleum industry.

Acetone is a colourless liquid which has a pleasant odour. It boils at 56° C. and dissolves in water in all proportions.

Acetone is an excellent solvent for a number of organic compounds. It is used in the manufacture of smokeless powders and cordite (a high explosive). Acetone serves as the starting material in the production of chloroform, $CHCl_3$, iodoform, CHI_3, and many other substances. It is also used in the manufacture of varnishes and paint and varnish removers. The use of acetone as a solvent for acetylene has already been mentioned in the chapter on the hydrocarbons.

3. Organic Acids

The general formula for organic acids is  $\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}H}$. R stands for an atom of hydrogen, or in most cases, an alkyl radical, and  $\mathrm{{-}\overset{\overset{O}{\|}}{C}{-}O{-}H}$, also written as COOH, is known as the *carboxyl radical.* It is important to remember that it is the hydrogen atom of this radical which is responsible for the acid properties of organic acids. For example, the hydrogen of the carboxyl radical can be replaced by metals to form salts. Thus,  $\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}O{-}H}$ is the formula for acetic acid, and only the hydrogen atom in the carboxyl group can be replaced by sodium to form the salt, sodium acetate,  $\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}O{-}Na}$.

Formic acid, HCOOH, is the first member of an homologous series of organic acids known as *fatty acids*, because many of them are prepared from fats. The formulas and names of several members of this series are given below.

$HCOOH$	Formic acid	Liquids
CH_3COOH	Acetic acid	
C_2H_5COOH	Propionic acid	
C_3H_7COOH	Butyric acid	

$CH_3(CH_2)_{14}COOH$ ....Palmitic acid } Solids
$CH_3(CH_2)_{16}COOH$.........Stearic acid }

Formic acid, the first member of the fatty acid series, occurs in nature, especially in nettles and ants. In fact the name of this acid was derived from the Latin word for ant, *formica.* The pioneer organic chemists obtained formic acid by distilling red ants. The irritating effect of a nettle sting and the bite of an ant are due partly to formic acid. The sting of a bee is also due to this acid. Formic acid is a colourless liquid which boils at 101° C.

The modern method of preparing formic acid is to heat sodium formate with the correct amount of sulphuric acid. Sodium formate is, in turn, obtained by heating carbon monoxide (from water gas) and sodium hydroxide, under pressure (6 to 10 atmospheres) and at a temperature of about 200° C. The equations for these reactions are:

$$CO + NaOH \longrightarrow \underset{\text{(sodium formate)}}{H{-}COONa}$$

$$2\,HCOONa + H_2SO_4 \longrightarrow 2\,HCOOH + Na_2SO_4$$

It will be remembered that when formic acid is heated with concentrated sulphuric acid, it decomposes into carbon monoxide and water according to the following equation:

$$\boxed{H}\,\boxed{CO}\,\boxed{OH} \xrightarrow[\substack{H_2SO_4\\ \text{(conc.)}}]{\text{heat}} H_2O + CO\uparrow$$

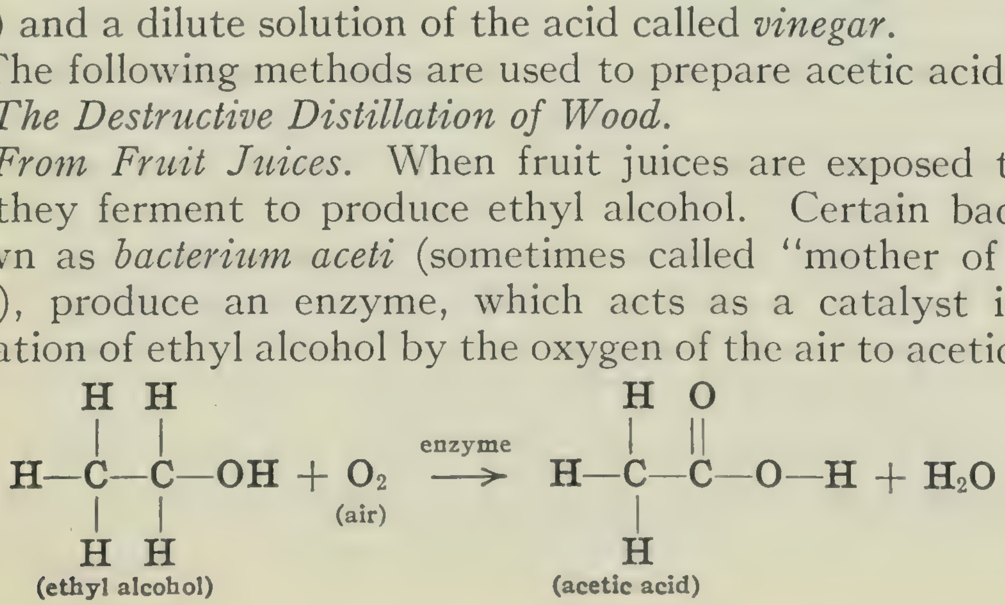
Formic acid is used to prepare certain special organic compounds in the laboratory and in industry. It is also used in the textile industry.

Acetic acid, CH_3COOH, is one of the most important of the organic acids from the industrial standpoint. It is encountered quite often in two forms, concentrated acetic acid (*glacial acetic acid*) and a dilute solution of the acid called *vinegar.*

The following methods are used to prepare acetic acid.

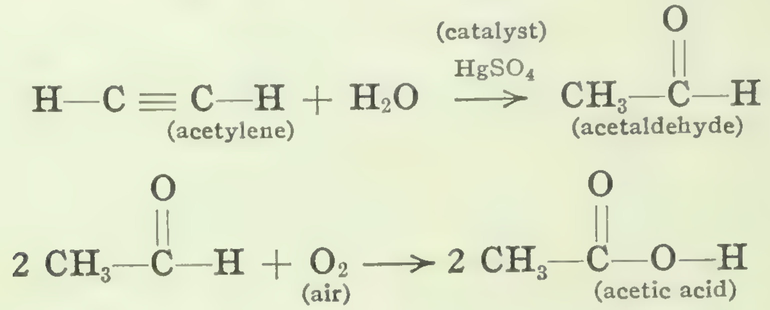
(1) *The Destructive Distillation of Wood.*

(2) *From Fruit Juices.* When fruit juices are exposed to the air, they ferment to produce ethyl alcohol. Certain bacteria, known as *bacterium aceti* (sometimes called "mother of vinegar"), produce an enzyme, which acts as a catalyst in the oxidation of ethyl alcohol by the oxygen of the air to acetic acid.



$$\underset{\text{(ethyl alcohol)}}{\begin{array}{c}\phantom{H{-}}H\;\;H\\ \phantom{H{-}}|\;\;\;|\\ H{-}C{-}C{-}OH\\ \phantom{H{-}}|\;\;\;|\\ \phantom{H{-}}H\;\;H\end{array}} + \underset{\text{(air)}}{O_2} \xrightarrow{\text{enzyme}} \underset{\text{(acetic acid)}}{\begin{array}{c}\phantom{H{-}}H\;\;O\\ \phantom{H{-}}|\;\;\;\|\\ H{-}C{-}C{-}O{-}H\\ \phantom{H{-}}|\\ \phantom{H{-}}H\end{array}} + H_2O$$

(3) *From Acetylene.* By means of a suitable catalyst, ($HgSO_4$) in dilute sulphuric acid, acetylene (C_2H_2) can be changed into acetaldehyde, which is oxidized by the air to acetic acid.



$$\underset{\text{(acetylene)}}{H{-}C{\equiv}C{-}H} + H_2O \xrightarrow{\substack{\text{(catalyst)}\\ HgSO_4}} \underset{\text{(acetaldehyde)}}{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H}$$

$$2\,CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H + \underset{\text{(air)}}{O_2} \longrightarrow \underset{\text{(acetic acid)}}{2\,CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}H}$$

Pure acetic acid (anhydrous) is an ice-like solid, melting at 16.7° C. This solid absorbs moisture from the air. Above its melting point, acetic acid is a colourless liquid, with a disagreeable odour; it boils at 118° C. Acetic acid is soluble in all proportions in water, alcohol, and ether. It is a weak acid because it only ionizes slightly when placed in water.

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

Of course, it shows all the properties which are common to acids.

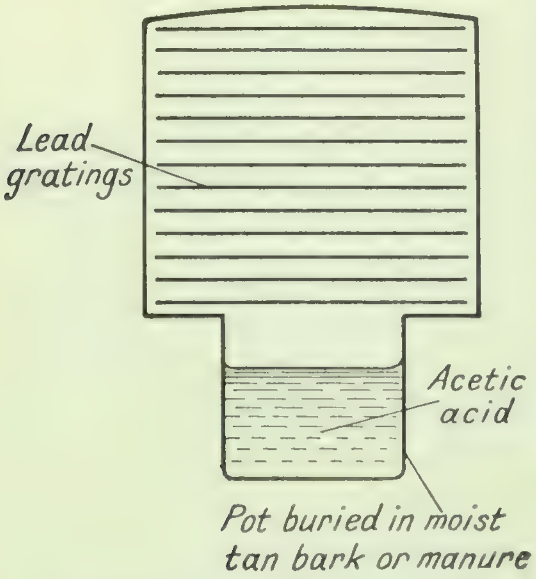


Fig. 202—The Manufacture of White Lead

Acetic acid is produced commercially at a relatively low cost, and so it has a great many uses. Ordinary vinegar is a dilute water solution of acetic acid (4 to 6 per cent). Acetic acid is used to make ethyl acetate, which is needed in the production of artificial silk. It is used in the manufacture of certain dyes and drugs. Acetic acid is used in the production of white lead (see Fig. 202), which is a very important component of most house paints. Of course, acetic acid is used to prepare acetates, such as lead acetate, $Pb(C_2H_3O_2)_2$, which is known as "sugar of lead" due to its sweet taste. It is very poisonous.

There are several organic acids which do not belong to the fatty acid series but they occur in certain common foods. The names, formulas, and occurrence of these are given in Table 27.

TABLE 27—SOME ORGANIC ACIDS FOUND IN CERTAIN FOODS

Name	Formula	Occurrence
Oxalic acid	$H_2C_2O_4$	rhubarb
Tartaric acid	$H_2C_4H_4O_6$	fruit juices
Citric acid	$H_3C_6H_5O_7$	lemons, oranges, grapefruit
Lactic acid	$HC_3H_5O_3$	sour milk

4. Esters

In a study of inorganic chemistry it is found that when an acid is added to a base, a salt and water are produced.

Acid + Base ⟶ Salt + Water

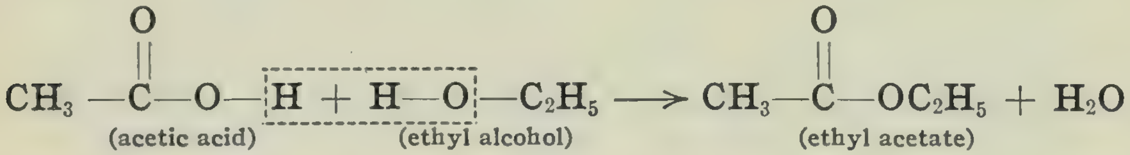
When an acid reacts with an alcohol, a compound, called an *ester*, and water are formed.

Acid + Alcohol ⟶ Ester + Water

This reaction is somewhat similar to the neutralization of an acid by a base, but it is considerably slower in speed since an alcohol does not ionize. Esters do not ionize, and so they are not salts. Both inorganic and organic acids react with alcohols to form esters. For example, nitric acid, a typical inorganic acid, reacts with ethyl alcohol to form the ester, ethyl nitrate.

$$C_2H_5\,OH + HNO_3 \longrightarrow \underset{\text{(ethyl nitrate)}}{C_2H_5NO_3} + H_2O$$

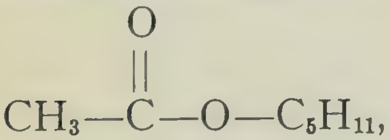
Acetic acid, a typical organic acid, reacts with ethyl alcohol to produce the ester, ethyl acetate.



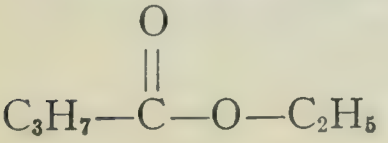
$$\underset{\text{(acetic acid)}}{CH_3-\overset{\overset{O}{\|}}{C}-O-}\boxed{H + H-O}\underset{\text{(ethyl alcohol)}}{-C_2H_5} \longrightarrow \underset{\text{(ethyl acetate)}}{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5} + H_2O$$

It is observed from the above equation that the ethyl radical, C_2H_5, has replaced the hydrogen atom in the carboxyl radical, —COOH, in acetic acid.

The esters of comparatively low molecular weight are liquids which have a pleasant, fruity odour. For example, amyl acetate,



$CH_3-\overset{\overset{O}{\|}}{C}-O-C_5H_{11}$, has a pear-like odour. Ethyl butyrate



$C_3H_7-\overset{\overset{O}{\|}}{C}-O-C_2H_5$ on the other hand, has the odour of pine-apples. Many esters are manufactured on a large scale in industry for use in the preparation of artificial perfumes and flavors. The chief use of esters is as solvents, such as those used in the preparation of quick-drying automobile lacquers.

5. Fats and Oils

Fats and oils (vegetable) are *esters* produced when fatty acids, usually of high molecular weight, react with glycerine.

$$\textbf{Glycerine} + \textbf{Fatty acid} \longrightarrow \underset{\text{(an ester)}}{\textbf{Fat or oil}} + \textbf{Water}$$

For example, when palmitic acid reacts with glycerine, the fat (an ester) known as *palmitin* (glyceryl palmitate) is formed.

$$\underset{\text{(palmitic acid)}}{3\ HC_{16}H_{31}O_2} + \underset{\text{(glycerine)}}{C_3H_5(OH)_3} \longrightarrow \underset{\text{(glyceryl palmitate)}}{C_3H_5(C_{16}H_{31}O_2)_3} + 3\ H_2O$$

From the above equation it is observed that this ester is formed by substitution of the replaceable hydrogen atom of the fatty acid by the glyceryl radical (C_3H_5). Table 28 gives the names, formulas and occurrence of some important fats and oils. It also gives the name and formula of the acid from which the fat or oil is derived. The fats given in this table make up most of the fats and oils in food and body fat. Stearin and palmitin are solids whereas olein is a liquid. The hardness of a fat depends upon the quantity of solid or liquid esters which are present. For example, beef tallow is made up of about 75 per cent palmitin and stearin and only about 25 per cent olein. It is one of the hardest of the fats found in nature. Lard is much softer and is easier to melt, because it is composed of about 60 per cent olein and about 40 per cent of palmitin.

TABLE 28—SOME IMPORTANT FATS AND OILS

Name	Formula	Occurrence	M.P. 0°C.	Acid from which Fat or Oil was Derived
Stearin (glyceryl stearate)	$C_3H_5(C_{18}H_{35}O_2)_3$	lard and beef tallow	71	Stearic acid ($HC_{18}H_{35}O_2$)
Palmitin (glyceryl palmitate)	$C_3H_5(C_{16}H_{31}O_2)_3$	lard and beef tallow	60	Palmitic acid ($HC_{16}H_{31}O_2$)
Olein (glyceryl oleate)	$C_3H_5(C_{18}H_{33}O_2)_3$	Olive oil	17	Oleic acid ($HC_{18}H_{33}O_2$)

Heating of a fat or oil with water at high temperature and pressure decomposes it into glycerine and the acid from which the fat was derived. This process is called hydrolysis.

6. Soaps

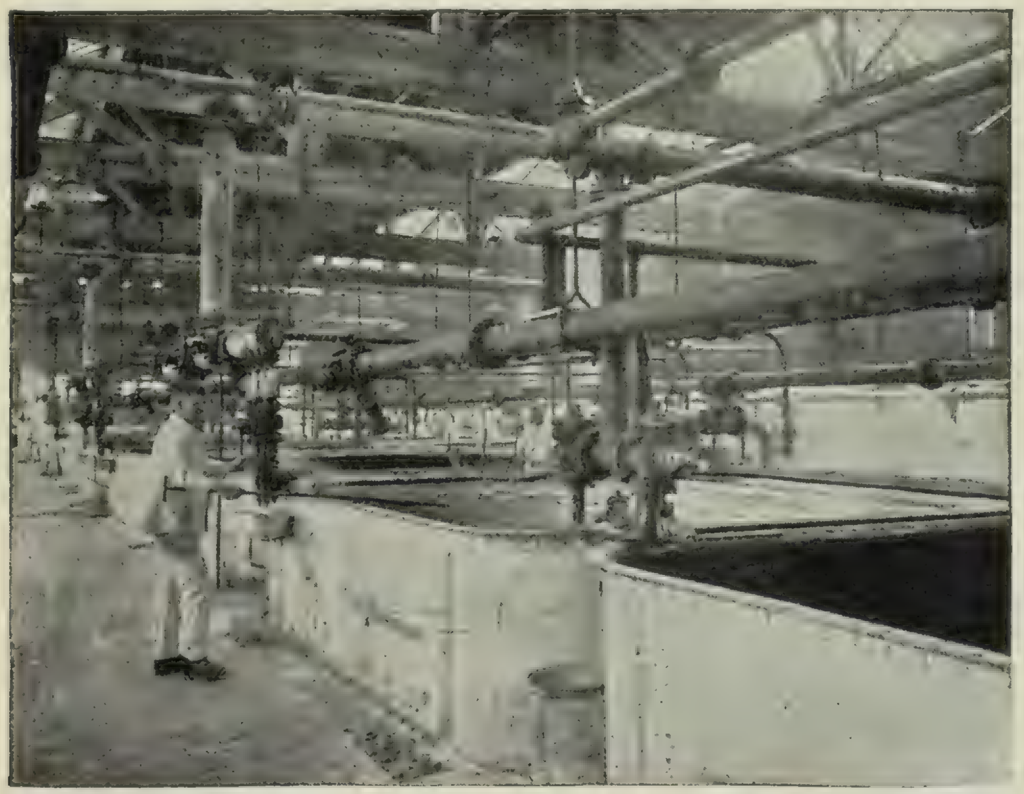
The production of soap has already been considered in a general way in previous chapters. The reaction involved in its preparation can be expressed simply by the following word equation.

Fat + Lye ⟶ Soap + Glycerine

Now that we know the formula for a fat we can write a molecular equation for the reaction between a fat and sodium hydroxide (lye).

$$\underset{\substack{\text{(palmitin,}\\ \text{an ester)}}}{C_3H_5(C_{16}H_{31}O_2)_3} + \underset{\text{(lye)}}{3\ NaOH} \longrightarrow \underset{\substack{\text{(sodium}\\ \text{palmitate, a soap)}}}{3\ NaC_{16}H_{31}O_2} + \underset{\text{(glycerine)}}{C_3H_5(OH)_3}$$

Sodium palmitate is the sodium *salt* of palmitic acid and it is a typical *soap*. *Soaps can be defined as the salts of palmitic, stearic and oleic acids.* The process by which soaps are made by decomposing the glyceryl esters of fatty acids is known as *saponification*. When sodium hydroxide is used in this process, the product is known as a *hard soap*. On the other hand, the use of potassium hydroxide produces a *soft soap*.

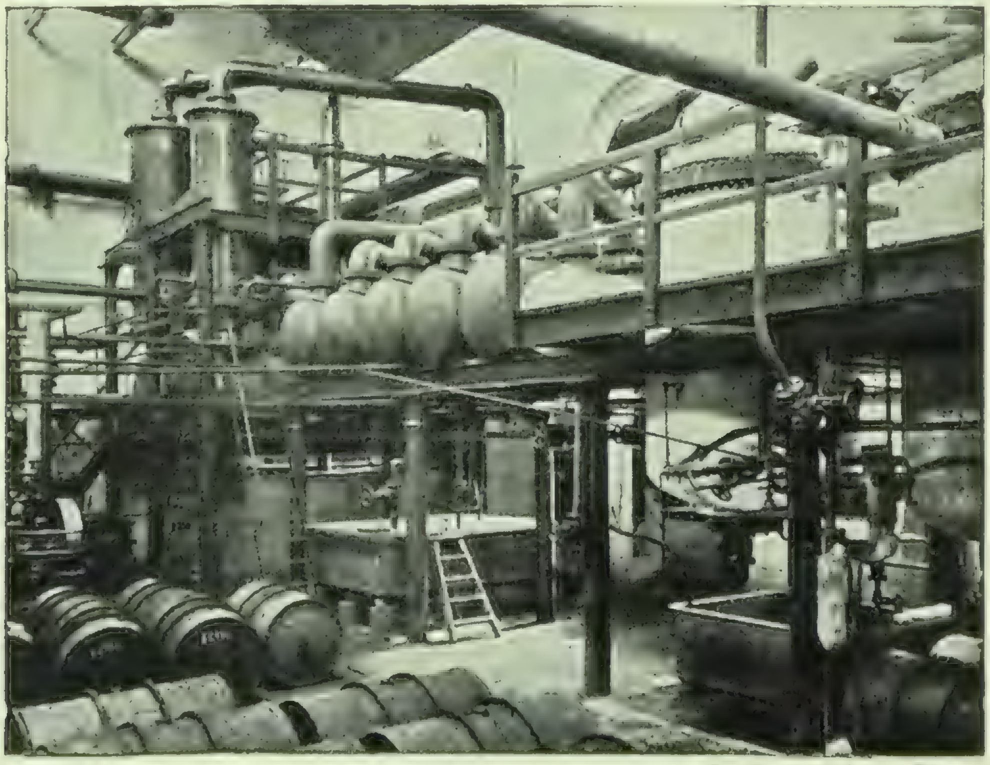


Courtesy of Lever Bros.

FIG. 203—SOAP BOILING IN HUGE KETTLES

Soap is made commercially on a very large scale. The oil or melted fat is poured into huge kettles (see Fig. 203) together with a solution of sodium hydroxide (lye). As a rule the kettles are very large, 500,000 pounds or more of soap being made in some of them in a single heating. The bottom of the kettle ends in a cone containing steam coils for heating the liquid. Live steam is forced into the bottom of the mixture to keep the fat and alkali well stirred. The saponification of the fats is completed in about one day. The soap is then suspended as very fine particles in the liquids present, or the chemist would say that the soap is in the form of a colloidal dispersion. To secure the soap in the solid state common salt (NaCl) is added and this process is known as "salting out." After the salt is added, the steam is turned off and the kettle allowed to stand for 4 to 12 hours. The soap rises to the top of the liquid as a curd-like material. The glycerine, produced as a by-product of the saponification reaction, settles to the bottom of the kettle and is withdrawn to be purified by distillation in a plant similar to the one shown in Fig. 204.

The crude soap is purified by washing and settling processes and is then run into the mixing machine called the *crutcher*. Here it is mixed with substances such as perfume, borax, water-



Courtesy of Lever Bros.

FIG. 204—GLYCERINE PLANT

glass, or washing soda. It is then run into large molds called *rames* to harden; afterwards it is cut and pressed into cakes of the desired size.

It is important that there is no free fat or oil in the finished product as their presence prevents the formation of a good lather. Of course, free lye (NaOH) is very harmful to the skin. It is necessary, therefore, that the correct amounts of fatty material (esters) and sodium hydroxide are brought together in order to produce a high grade soap.

Soap forms with water a mixture known by chemists as a colloidal dispersion. The solid particles in such a system have the property of holding on their surfaces certain other particles. This phenomenon is known as *adsorption*. When soap is used to remove dirt from the skin or from cloth, the colloidal soap particles adsorb the dirt particles. Thus, when the soap is carried away by water, the dirt particles go with it. Grease is removed from skin or cloth because soap is an emulsifying agent. That is, it converts the grease on skin or cloth into very small droplets which are swept away by an excess of water.

Much of the soap used in homes contains a certain amount of rosin which makes the soap more soluble in cold water and increases its ability to form a lather. Floating soaps owe their lightness to bubbles of air and naphtha soaps containing about 5 per cent of petroleum naphtha. Transparent soaps are produced by the addition of glycerine or sugar. Castile soaps are made from olive oil. Scouring soaps contain from 5 to 10 per cent of soap and from 80 to 90 per cent of some gritty material, such as fine sand or volcanic ash. Soaps are made attractive by the addition of various colouring materials and perfumes. For example, the colour of mottled soaps is produced by the addition of Prussian blue or some similar pigment. Soap powders contain only about 10 to 20 per cent of ordinary soap ground to a fine powder. The other part of the soap powder is made up of sodium carbonate, Na_2CO_3, (washing soda) and sodium phosphate, Na_3PO_4.

EXERCISES

1. (a) What is an aldehyde?
   (b) Write the structural formulas for two simple aldehydes.
2. (a) Write the equation for the preparation of formaldehyde.
   (b) What is formalin? Mention three uses of this substance.
3. Write a short note on "bakelite."

4. (a) What is a ketone?
   (b) Give three uses of acetone.
5. (a) What are organic acids?
   (b) Give the names and formulas for three organic acids.
6. (a) Write the equations for the reactions used in the modern method of preparing formic acid.
   (b) Why was formic acid used in the laboratory preparation of carbon monoxide?
7. (a) Give three methods of preparing acetic acid.
   (b) Tabulate five properties of acetic acid.
   (c) Make a list of five uses of acetic acid.
8. (a) What is an ester?
   (b) How does an ester differ from a salt?
   (c) Give the name, formula and odour of two esters.
   (d) Mention two uses of esters.
9. (a) What is a fat?
   (b) Give the name, formula and occurrence of two important fats.
   (c) Why is lard softer than beef tallow?
10. (a) What is a soap?
    (b) What is meant by the term saponification?
    (c) What is the difference between a hard and a soft soap?
11. (a) Write a short note on the commercial production of soap.
    (b) What two substances should not be present in a good soap? Explain why these materials are harmful.
12. Explain how soap removes dirt and grease from skin or cloth.
13. Write a note on domestic soaps and soap powders.

CHAPTER L

THE CARBOHYDRATES

Carbohydrates are organic compounds containing the elements carbon, hydrogen and oxygen. The hydrogen and oxygen are usually present in these compounds in the same proportion as they are in water, two atoms of hydrogen for every atom of oxygen. For example, the formula for cane sugar is $C_{12}H_{22}O_{11}$. The pioneer organic chemists thought that these compounds were hydrates of carbon, so they called them carbon hydrates, and later, carbohydrates. Thus, they wrote the formula for cane sugar as $C_{12}(H_2O)_{11}$. Of course, it was soon discovered that the carbohydrates are not hydrates, but they make up an interesting and important group of organic compounds.

The carbohydrates can be classified into three main groups. These are the *sugars*, such as cane sugar; the *starches*, such as corn starch; and the *celluloses*, such as that obtained from wood. Each of these groups will now be considered briefly.

1. The Sugars

(1) CLASSIFICATION. The sugars are those carbohydrates which are crystalline and have a sweet taste. A simple classification of the sugars is based upon their reaction to a solution, known as *Fehling's solution*. This solution is made by mixing two solutions, usually known as Fehling's solutions numbers 1 and 2. Solution number 1 is made by dissolving copper sulphate crystals ($CuSO_4 . 5H_2O$) in water. Solution number 2 is prepared by dissolving sodium potassium tartrate (Rochelle salts), $NaKC_4H_4O_6 . 4H_2O$, and sodium hydroxide in water. The solutions are kept separately and not mixed until time for use, because the mixed solution deteriorates while standing. When equal quantities of Fehling's solutions numbers 1 and 2 are mixed, a solution with a deep blue colour is obtained. If several drops of a glucose solution is added to this solution, and the mixture is heated, the blue colour disappears. The copper sulphate in the solution is reduced to cuprous oxide (Cu_2O) by the glucose, which is a reducing agent. Since cuprous oxide is insoluble, it is precipitated in the form of a red or a yellow solid. Certain other sugars, such as fructose, also reduce

Fehling's solution in this way, and they are known as *reducing sugars.* On the other hand, some sugars, such as cane sugar (sucrose), do not reduce Fehling's solution, and so they are known as *non-reducing sugars.*

(2) GLUCOSE, $C_6H_{12}O_6$. This sugar is also known as *dextrose* or *grape sugar.* Glucose is present in the juices of many fruits. It can be made from certain sugars and from starch. For example, cane sugar (sucrose) can be decomposed by hydrolysis into glucose and its isomer, fructose (levulose).

$$\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\substack{\text{(glucose}\\ \text{or}\\ \text{dextrose)}}}{C_6H_{12}O_6} + \underset{\substack{\text{(fructose}\\ \text{or}\\ \text{levulose)}}}{C_6H_{12}O_6}$$

Acids act as catalysts in this reaction. In digestion of cane sugar in the body, enzymes serve as catalysts, breaking down sucrose into the simpler sugars.

The boiling of corn starch with a water solution of hydrochloric acid under pressure produces a substance known as "corn syrup" or commercial "glucose." This product is a solution consisting of dextrose (glucose), maltose, and dextrin in varying proportions. The formula for starch can be represented as $(C_6H_{10}O_5)_x$ and the acid serves as a catalyst in the hydrolysis of the starch.

$$\underset{\text{(starch)}}{(C_6H_{10}O_5)_x} + x\ H_2O \longrightarrow x\ \underset{\text{(glucose)}}{C_6H_{12}O_6}$$

Corn syrup is used to a considerable extent in bakeries to sweeten pastries, in the manufacture of candies, as a food in the home, and as a syrup for the sweetening of various confections. It is also sometimes fermented to produce ethyl alcohol.

It is interesting to know that all starches and sugars are changed into glucose, or one of its isomers, during the process of digestion. Glucose, without further change, goes through the walls of the intestines into the blood stream, which takes it to the various parts of the body. When a person is in good health, the blood contains about 0.1 per cent of glucose.

(3) CANE SUGAR (SUCROSE), $C_{12}H_{22}O_{11}$. Cane Sugar, known by the chemist as sucrose, is the most important commercial sugar. In a normal peacetime year the world produces and uses about 35,000,000 tons of sugar. Sugar is used considerably by research and industrial chemists in the production of many useful articles of commerce.

Most sugar comes from either the sugar cane or the sugar beet. There is no chemical difference between refined cane sugar and refined beet sugar. They are both almost pure sucrose (99.85 per cent). Maple sugar, which contains about 85 per cent sucrose, is produced in considerable amounts in certain areas in Canada and the United States. The sugar found in milk is known as *lactose.* The sugar *maltose* is obtained by treating starch with malt. Lactose and maltose are isomers of sucrose, and so they can also be represented by the molecular formula $C_{12}H_{22}O_{11}$.

As the methods of producing sucrose from sugar cane and from sugar beets are fundamentally the same we shall consider in detail only one method, the sugar cane process.

The first stage of the process consists of crushing the sugar canes (containing 15 per cent sucrose), grown in tropical and sub-tropical climates, between steel rollers. This operation gives a juice containing impurities which must be removed. To do this the juice is treated with slaked lime, $Ca(OH)_2$, which neutralizes acidic impurities and also removes some of the other impurities as a precipitate. The sugar solution is separated from the precipitate by filtration and the filtrate is then evaporated in vacuum pans (see Fig. 157, page 308) at a temperature of about 65° C. Evaporation at this comparatively low temperature prevents the sugar from charring. As the water is driven off, the solution becomes more concentrated, and, as it cools, dark brown sugar crystals come out of the solution. These crystals are separated from the "mother liquor" (molasses) by centrifugal machines. The mixture which is left behind when the sugar crystals are removed, is called molasses and still contains much sucrose. The dark brown sugar obtained in this way is known as *crude* or *raw sugar.*

The analysis of a typical sample of crude sugar is shown below:

Sucrose (cane sugar)	96%
Glucose (dextrose)	1%
Water	1%
Mineral substances	0.5%
Organic impurities	1.5%

The raw sugar is next shipped to a sugar refinery, usually located in a large city, for conversion into white granulated or soft sugars.

The first step in the refinery is the washing of the sugar.

Each grain of the raw product is surrounded by a fine film of molasses, which must be first removed by a process known as *affination*, which consists of mixing the crude sugar with a syrup obtained from washing raw sugar with water. The next stage of the cleaning process consists of spinning the mixture in large baskets called centrifugals, and applying water until the crystal is clean.

This washed sugar is then dissolved in hot water to form a heavy syrup containing about 65 per cent sugar. To this is added kieselguhr, a light inert earth, which forms a porous layer on the filtering apparatus, and so assists in the filtering operation. The mixture of sugar syrup and kieselguhr is then forced through large filters under pressure, where the earth and all the undissolved impurities are removed, coming out as a bright but highly coloured liquid.

The next step is the purification of this liquor. This is done by running the liquor through large cisterns filled with bone-char (bone-black), which adsorbs the coloured impurities. Thus, as the sugar solution runs out of the bone-char cisterns, it is water white and sparkling.

The sugar solution now goes to the vacuum pans to be boiled to secure the crystalline sugar. The vacuum pan is a large kettle, closed so that a partial vacuum can be obtained, and filled with heating coils. As the water is evaporated off, crystals commence forming and they gradually increase in quantity and size. When the crystals are of the right size, the adhering syrup is spun off in centrifugals and then washed with hot water. The sugar, containing 3 to 3.5 per cent of water, is next sent to the granulators (dryers) to remove the water.

The drying takes place in large horizontal drums through which a current of hot air passes. The sugar goes from the granulators to the screeners, where it is classified according to the size of its crystal. Then it is sent to the packing department, where it is packed into cartons, bags and barrels.

The average person does not realize the importance of sugar in our everyday life. In normal times every person in Canada consumes an average of one third of a pound of sugar per day in some form or another. The daily production of a large sugar refinery is over a million pounds of sugar.

Sucrose does not reduce Fehling's solution, and so it is classed as a non-reducing sugar. When cane sugar is heated to a temperature of about 210° C., it is decomposed into a brown substance known as *caramel.* Caramel is used to a considerable extent in the preparation and flavouring of candies and confections.

The chief use of sugar is as a food but it is used in many other ways. For example, sugar is used in the manufacture of the following substances: acetone, alcohol, adhesives, beverages, bread, candy, cereal products (breakfast cereals), cocoa, ice cream, drugs, explosives, glycerine, hides (tanning), jams, jellies, leather, oxalic acid, rubber (synthetic), soaps, and water proofing materials.

2. The Starches, $(C_6H_{10}O_5)_x$

Starch occurs in all green plants and it is the most abundant of all foods. For commercial purposes starch is usually obtained from potatoes, corn, rice, wheat, arrowroot, etc., by washing the starch granules out of the various parts of the plant with water.

FIG. 205—HARVESTING OF WHEAT IN SASKATCHEWAN
Wheat furnishes much of the starch in our foods.

Starch is insoluble in cold water. When heated in water, the starch granules swell and in time break, and the starch is scattered throughout the liquid as a colloidal dispersion (a very fine suspension). If this mixture is thick enough, it is called a *starch paste.* The starch molecule is very large, and since it does not change to a gas on heating or form a true solution, chemists cannot determine its true molecular weight. Its formula is usually written as $(C_6H_{10}O_5)_x$, where x represents an unknown value. We know that the molecule is built up somehow of $C_6H_{10}O_5$ units, but we do not know for certain how many of these units are joined together in the starch molecule. Free iodine turns starch blue in colour, and this fact is used as a chemical test for both free iodine and starch.

When starch is heated to 200-250° C., it is changed into a substance, possessing simpler molecules, called dextrin. Dextrin is a sticky material when wet, and it is used in making mucilage for envelopes and postage stamps. Dextrin is formed during the baking of bread. The surface of the loaf is subjected to a higher temperature than the interior, and so the starch on the crust is changed into dextrin, which is sweeter than the central portion of the loaf.

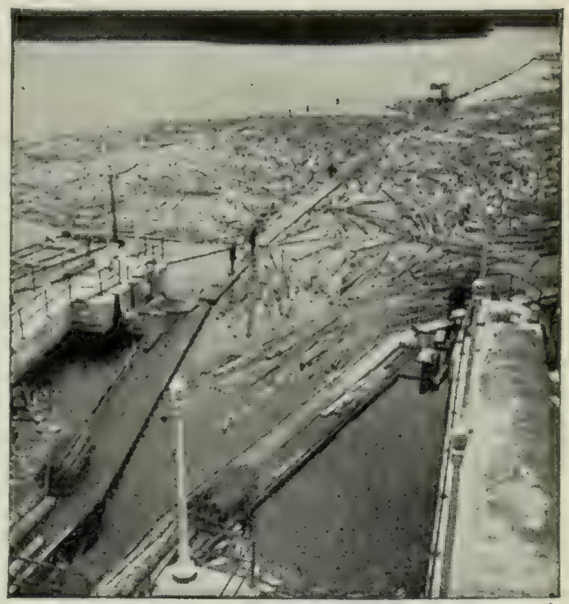
Starch has many important uses. Its chief use, of course, is as a food. It is also used in the manufacture of commercial glucose (corn syrup). Another important use of starch is in the production of ethyl alcohol. Much starch is used in laundry work. Starch paste is used in hanging wall paper. The textile, paper and foundry industries also use considerable quantities of starch.

3. The Celluloses, $(C_6H_{10}O_5)_x$

The carbohydrate known as cellulose makes up the chief part of the cell walls of plants. It occurs in relatively pure form in the seed hairs of the cotton plant. Cotton obtained from this source is about 85 per cent cellulose, and the materials making up the remaining 15 per cent can be easily removed by certain solvents, leaving the pure cellulose. Absorbent cotton is almost pure cellulose. The filter paper used in the laboratory is another good example of almost pure cellulose. Most of the cellulose used in industry is obtained from cotton and wood. The long fibres in wood are cemented together by a gummy substance called *lignin*.

Cellulose is insoluble in water and all other ordinary solvents. However, certain chemicals can convert cellulose into soluble compounds. For example, it has been found that when cellulose is treated with sodium hydroxide (lye), a compound is produced which is soluble in carbon disulphide (CS_2). This reaction is the basis of the production of most of the rayon made in America. Cellulose is an indigestible substance.

Cellulose dissolves slowly in concentrated sulphuric acid. When this solution is diluted with water and then boiled, glucose is produced as the final product.



Courtesy of The E. B. Eddy Co. Ltd.

FIG. 206—PULPWOOD LOGS ARE BEING GUIDED INTO A PULP MILL

Cellulose has many important industrial uses. Perhaps the most important one is its use in the *manufacture of paper*, which is so important in our modern civilization. Newsprint paper, the paper used to print newspapers, is made entirely from wood. The woods used to make paper are white and black spruce with a small percentage of balsam. The average of a number of experiments to determine the chemical composition of spruce wood gave the following values:

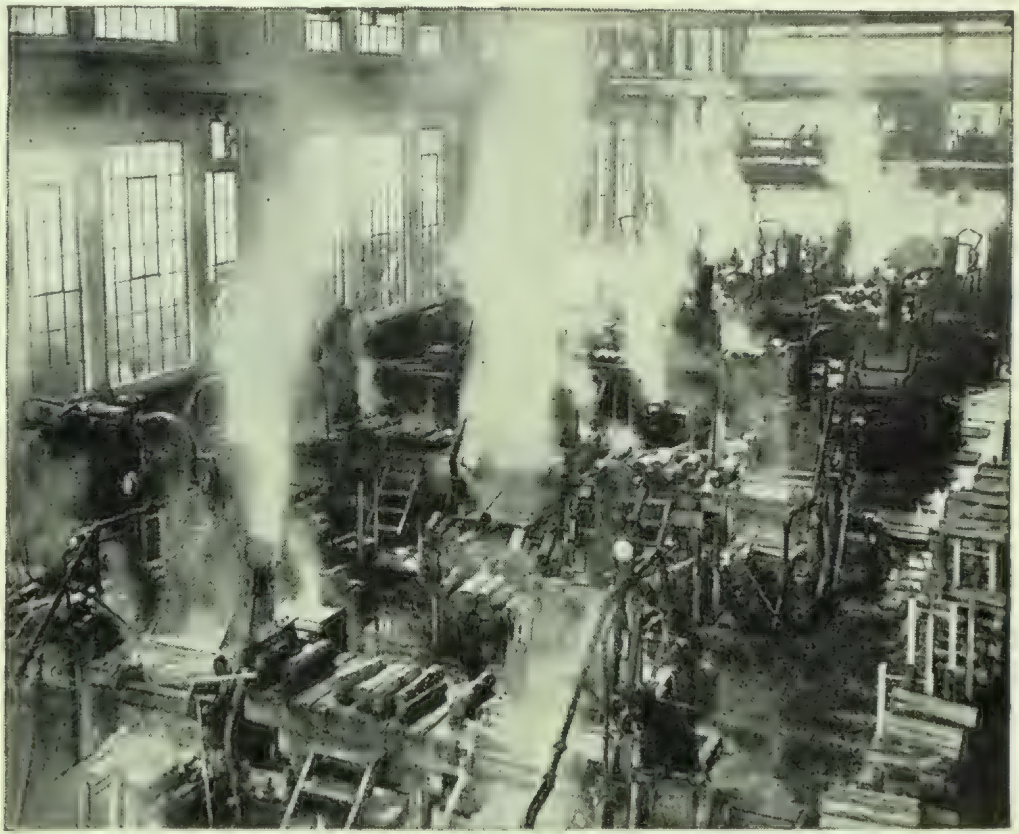
Cellulose	53%
Other carbohydrates	14%
Lignin	29%
Protein	0.7%
Resins and fats	3.3%

The first step in the manufacture of paper is the conversion of the wood to a pulp. There are two chief types of pulp used—mechanical or groundwood pulp, and chemical or sulphite pulp. Groundwood pulp contains nearly all of the wood in fibre form and is used as much as possible because of its cheapness. Sulphite pulp is almost pure cellulose. It is made up of longer and stronger fibres and, of course, it is more expensive to produce than the groundwood pulp.

The first step in the preparation of wood for making paper is to saw the logs into short lengths, varying from 24 inches to 48 inches, depending on the width of the grinding stones used to make the pulp. The bark on the logs is removed by friction in large revolving steel drums, and the wood is then ready to be changed into pulp.

GROUNDWOOD PULP. Groundwood pulp is made by pressing blocks of wood against large grindstones, which are revolving at about 250 revolutions per minute. During the grinding, the curved side-surface of the log is pressed against the grindstone at a pressure of 25 to 30 pounds per square inch, and water is sprayed on the surface of the stone to wash away the fibres and to keep the stone and pulp from becoming too hot.

It must be remembered that groundwood pulp contains not only cellulose but all other parts of the wood, such as lignin and resin. As the pulp leaves the grinder, it consists of about 5 per cent wood fibre and 95 per cent water. This pulp is thinned down, by the addition of water, to about one per cent wood fibre, and is passed through screens with ⅜″ holes to remove the slivers and coarse fibres. It is then pumped through finer screens, and the fibres suspended in water which pass through are used for making newsprint paper. The material which does not pass through the screens, is subjected to a refining process; it is then screened again to obtain all the good fibres.



Courtesy of The E. B. Eddy Co. Ltd.

FIG. 207—THIS PICTURE SHOWS A BATTERY OF GRINDERS MAKING GROUNDWOOD PULP. A SUPPLY OF LOGS MAY BE SEEN BESIDE EACH GRINDER. WHAT IS CAUSING THE STEAM?

Groundwood pulp is used not only to make newsprint paper but also to produce the cheaper grades of paper, such as wall paper, wrapping paper, cardboard, and insulating wall boards. In the production of these papers, as in "newsprint" paper, some sulphite pulp is mixed with the groundwood pulp. The composition of such papers is about 80 per cent groundwood and 20 per cent sulphite pulp.

SULPHITE PULP. Sulphite pulp is almost pure cellulose. It is produced by treating wood with certain chemicals which dissolve the lignin and other substances in the wood and do not affect the cellulose.

The first step in producing sulphite pulp is to chip the wood in a chipper, which is an eight foot disc set with knives. The chips produced by the machine are about one inch square and one eighth of an inch thick.

The next step is the preparation of the calcium bisulphite liquor to cook the chips. Sulphur, imported from Texas or Louisiana, is melted in a tank equipped with steam coils. The molten sulphur is fed into a special type of burner where it combines with the oxygen of the air to form sulphur dioxide gas (SO_2). The sulphur dioxide is cooled to a temperature of about 20° C. and pulled by a fan into the bottom of tall concrete towers. These towers are filled with roughly crushed limestone (calcium carbonate, $CaCO_3$) and water is continually trickling from a spray at the top of the towers. The water and sulphur dioxide react to form sulphurous acid.

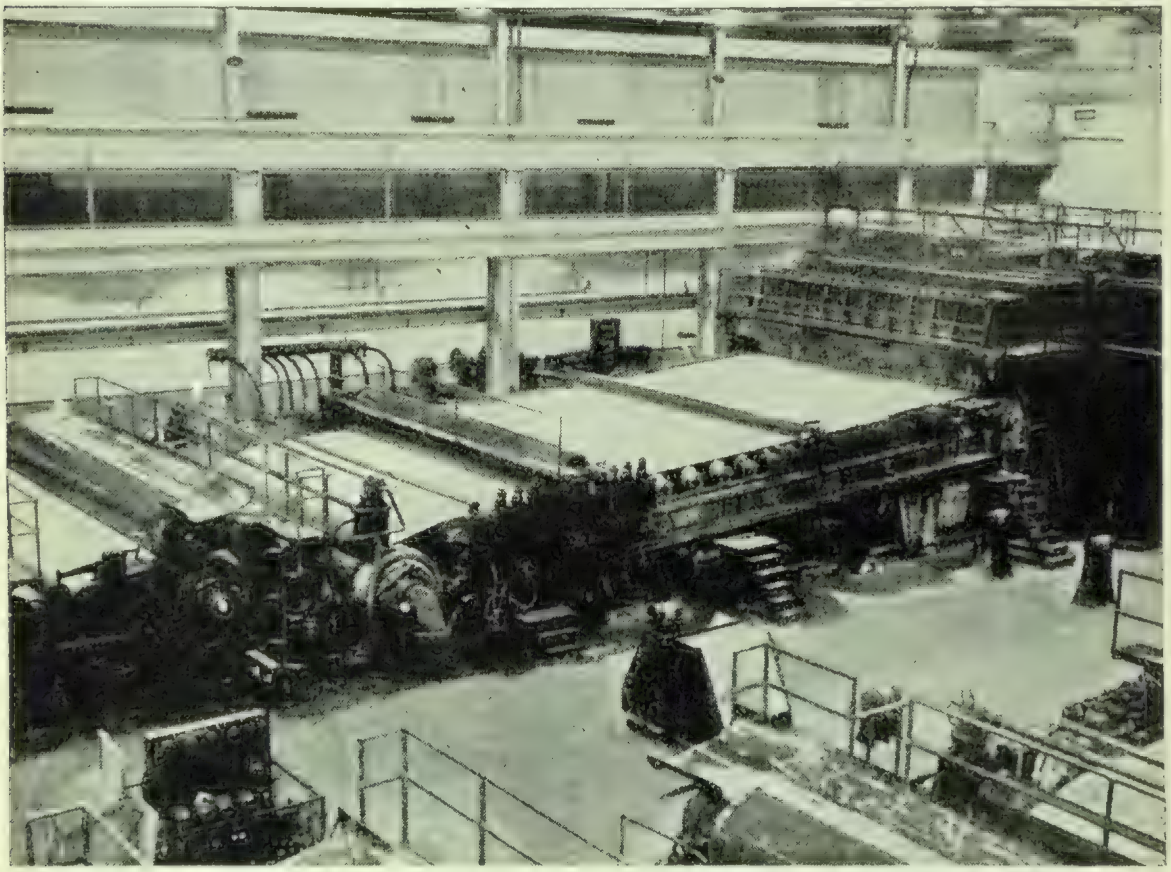
$$H_2O + SO_2 \rightleftharpoons H_2SO_3$$

The sulphurous acid reacts with the limestone to produce the calcium bisulphite liquor, which is used in cooking the chips.

$$CaCO_3 + 2\ H_2SO_3 \longrightarrow Ca(HSO_3)_2 + H_2CO_3$$
$$H_2CO_3 \longrightarrow H_2O + CO_2\uparrow$$

The next process is to place the wood chips into large tanks, known as digesters, usually about 15 feet in diameter and 50 feet high and lined with acid resisting brick. The cooking liquor is pumped into the digester and fills the spaces between the chips. The mixture in the digester is then heated by steam for eight to ten hours. This treatment dissolves most of the lignin, leaving in suspension almost pure cellulose. At the end of the cooking period a valve at the bottom of the digester is opened and the pressure on the digester forces the pulp into containers known as *blow pits*. These blow pits are large circular tanks with perforated bottoms which allow the digester liquor, containing about one-half of the original weight of the wood, to drain off. This sulphite pulp is then thoroughly washed with water to remove all traces of the bisulphite solution, diluted with water and screened, in much the same way as is the groundwood pulp.

THE MANUFACTURE OF PAPER. The groundwood and the sulphite pulps are thickened by filters and pumped to the automatic mixers which regulate the proportion of groundwood and sulphite going to the paper machines. As already mentioned, the mixed pulp contains about 80 per cent groundwood and 20 per cent sulphite pulp; the latter is added to furnish strength and pliability to the pulp when going over the paper machine. The pulp is next diluted to a consistency of 0.45 per cent fibre and flows through a narrow opening on to an endless copper wire screen, known as the *fourdrinier wire*. This wire quickly carries the water and suspended pulp towards the paper machine, and as it travels the water drains off, leaving the small cellulose fibres interlaced on the wire like a mat. The moisture content of the formed sheet is reduced still more by a suction

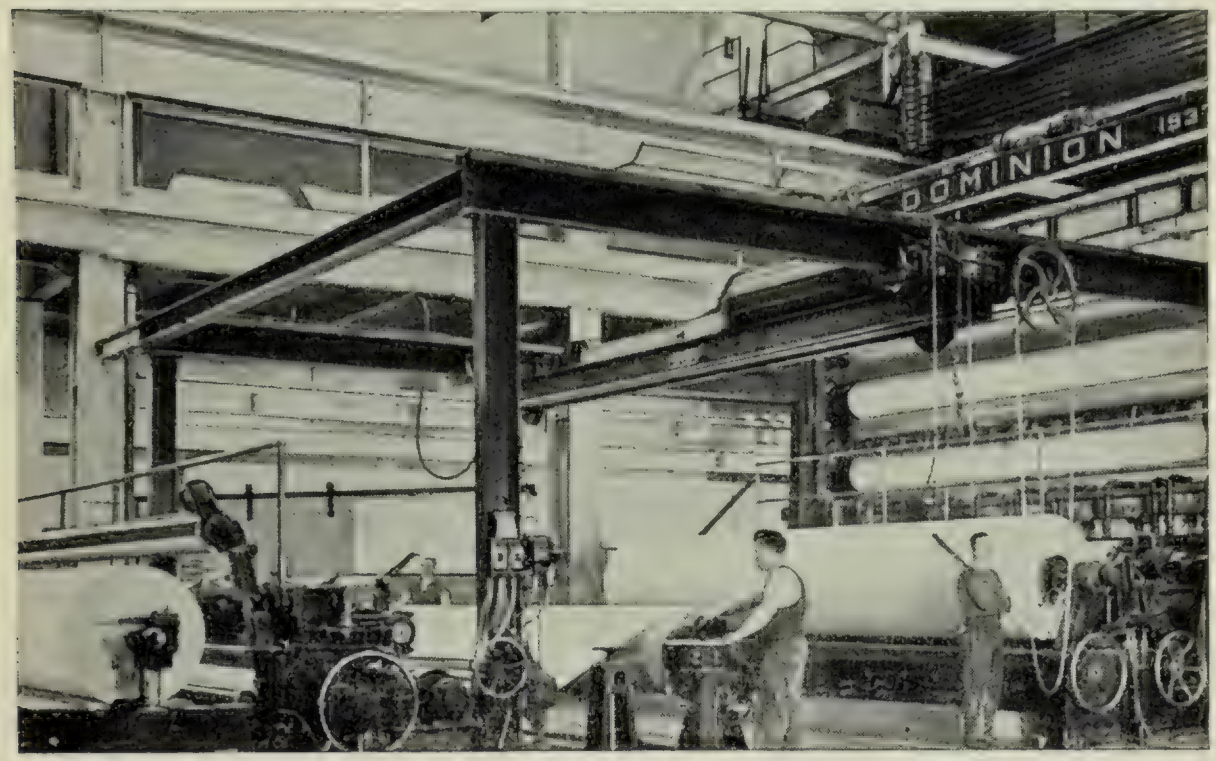


Courtesy of Dominion Engineering Co. Ltd.

FIG. 208—THIS IS A GENERAL VIEW OF THE WET END OF A PAPER MACHINE. THE PULP IS FLOWING FROM THE HEAD BOX, AT THE RIGHT, ON TO THE WIRE. AT THE LEFT, THE SHEET OF WET PAPER IS LEAVING THE WIRE AND PASSING BETWEEN THE PRESS ROLLS

roll and vacuum boxes near the end of the wire. The sheet is then carried by felts through suction presses, where more water is removed, reducing the moisture content to about 70 per cent of the original weight.

The next stage of the process is that of *drying*. The wet sheet leaving the presses is carried on endless cotton dryer felts around 30 to 48 cylinders of 5 to 6 feet in diameter, containing steam at 5 to 15 pounds pressure. The sheet as it leaves the dryers has a moisture content of about 8 per cent. The sheet is rough on the surface and to make it smooth it is passed through what is known in the paper industry as a *calendar stack*. This consists of a bank of heavy steel rolls one above the other, the bottom roll being driven. The final step consists of winding the paper on a reel and transferring it to the winder, where it is cut into the width required by the printer. It then goes to be wrapped for protection in shipping.



Courtesy of Dominion Engineering Co. Ltd.

FIG. 209—THIS VIEW OF THE DRY END OF A PAPER MACHINE SHOWS, FROM RIGHT TO LEFT, THE CALENDER, REEL AND WINDER

The pulp and paper industry is a very important one, having a direct and important influence on many other Canadian industries, such as power development, transportation, mining and farming. About half a million people depend directly upon the pulp and paper industry for a living, and it leads all manufacturing industries of Canada in the amount it pays out in salaries and wages. The amount of money invested in this industry is larger than that of any other manufacturing industry. Quebec is the largest producer of paper in Canada, its output being nearly double that of Ontario.

Fig. 210—Rolls of Newsprint Ready for Shipment

Cellulose has many other important uses in addition to being our chief source of paper. When cellulose is treated with a mixture of nitric acid and concentrated sulphuric acid, a substance known as *nitrocellulose* (cellulose nitrate) is produced. Nitrocellulose is a mixture of various nitric acid esters of cellulose. The properties of any given type of nitrocellulose depend upon the percentage of nitrogen contained in the substance. For example, *guncotton* is a nitrocellulose which contains about 13.5 per cent of nitrogen; it has properties different from *pyroxylin* which contains from about 11 to 12.5 per cent of nitrogen. Guncotton is used in the production of smokeless powders, cordite, gelatin dynamites, and other high explosives.

Pyroxylin has many important commercial uses. It is used in the manufacture of *photograph films*. It is also the basic material in all the *lacquers* which have been used so much in recent times, especially in the automobile industry. Imitation leather used for bookbinding, automobile cushions, hand bags, and trunks consist of a canvas base coated with pyroxylin.

Collodion is a solution of pyroxylin in a mixture of ethyl alcohol and ether. Celluloid and similar substances are mixtures of pyroxlin and camphor. It is well to remember that celluloid is inflammable because many serious accidents have resulted from bringing it near a hot flame.

Cellulose is also used in the production of such important textiles as rayon and mercerized cotton. Cellophane is also made from cellulose.

EXERCISES

1. (a) What is a carbohydrate?
   (b) What are the chief classes of carbohydrates? Give one example of each.
   (c) Distinguish between a non-reducing and a reducing sugar. Give one example of each.
2. Discuss glucose under: (1) Occurrence, (2) Preparation, (3) Uses.
3. Write a short essay on the refining of cane sugar.
4. Tabulate ten uses of sucrose.
5. Discuss starch under: (1) Occurrence, (2) Preparation, (3) Properties, (4) Uses.
6. Write a short essay on cellophane under: (1) Occurrence, (2) Properties, and (3) Uses.
7. Discuss the use of cellulose in the manufacture of paper under:
   (1) Groundwood pulp;
   (2) Sulphite pulp;
   (3) Paper manufacture;
   (4) Importance of pulp and paper industry.
8. (a) What is nitrocellulose?
   (b) Give two important types of nitrocellulose.
   (c) Give three uses of gun-cotton.
   (d) Tabulate five uses of pyroxlin.
   (e) What textiles are made from cellulose?

CHAPTER LI

SOME OTHER IMPORTANT ORGANIC SUBSTANCES

1. Foods

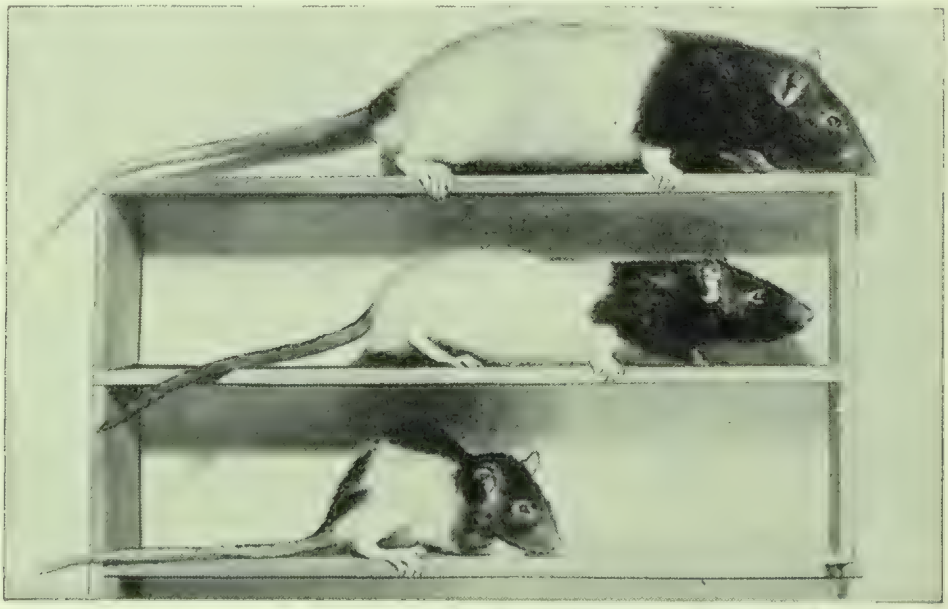
Foods are materials which are taken into the body to do the following things:

(1) To supply the body with the necessary substances to build up new tissues and to repair worn out tissues.

(2) To furnish the body with the energy which is necessary in order that we may do our work. Energy in the form of heat is also needed to keep the body at its normal temperature (about 98.6° F.).

Foods are classified into five groups. These are the carbohydrates, fats, proteins, mineral salts, and vitamins. In addition, oxygen and water, although not usually considered as foods, are necessary to keep the body alive.

(1) THE CARBOHYDRATES. The carbohydrates, which are used as foods, are the sugars and the starches. The starches are



Courtesy of Canadian Medical Association

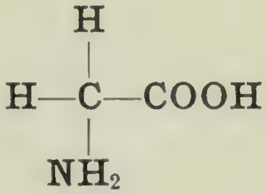
FIG. 211

Here is a picture of three rats. The upper one was fed a completely adequate diet. The middle rat received only about two-thirds the proper amount of protein. The lower rat had all the food it could eat, but containing less than one-third the proper amount of protein. This rat is sick; growth has completely stopped.

present in cereals, rice, potatoes and bread. The sugars and starches are energy foods; they are eaten in large quantities by people who are doing heavy manual work or who work outdoors. Sugars supply the body with energy very rapidly; thus, for example, long distance runners eat sugars at regular periods during a race. The carbohydrate foods also help in producing fats in the body.

(2) Fats. The fats are organic compounds containing the elements carbon, hydrogen and oxygen. They occur in many common foods such as milk, butter, fat of meat, and nuts. Fats, like carbohydrates, are energy foods. To a certain extent they form layers of protective tissue which may serve the body under certain conditions as a reserve food supply.

(3) Proteins. The proteins are very complex organic compounds containing the elements carbon, hydrogen, oxygen, and *nitrogen*. They are built up of units known as amino acids, and there are about 20 different kinds of these units. The simplest amino acid is glycine, also known as *glycocoll*. Its structural formula is shown below.



$$\mathrm{H{-}\overset{\displaystyle H}{\overset{|}{\underset{\underset{\displaystyle NH_2}{|}}{C}}}{-}COOH}$$

(glycine)

Proteins are present in the white of egg (albumen), gelatin, gluten of wheat, lean meat, milk (casein) and legumes. The chief functions of proteins are to build and repair the body tissues.

(4) Mineral Salts. When a food is heated very strongly, a small quantity of an ash is left. This ash contains inorganic compounds known as the mineral salts of foods; they are of great importance to the proper functioning of the body. Scientists have recently discovered that small quantities of 13 mineral elements are essential to growth and good health.

Calcium is an element which, though sometimes lacking in the diet of many people, is necessary to the formation of good bones and teeth. It should be present especially in the diet of children. The following foods are among the chief sources of calcium: cheese, milk, egg yolk, beans, wheat bran, nuts, dried figs, and leafy vegetables such as cabbage, especially the outermost leaves.

Iron is another important mineral food; lack of this element in the diet is responsible for one form of anaemia. Iron is required in the formation of red blood cells, and it can be obtained by eating meats (especially liver, heart and kidney), whole-grain cereals, beans, figs, spinach, asparagus, molasses and oatmeal.

Iodine, also, is needed in small amounts to enjoy good health. In most places natural water contains sufficient iodine to furnish

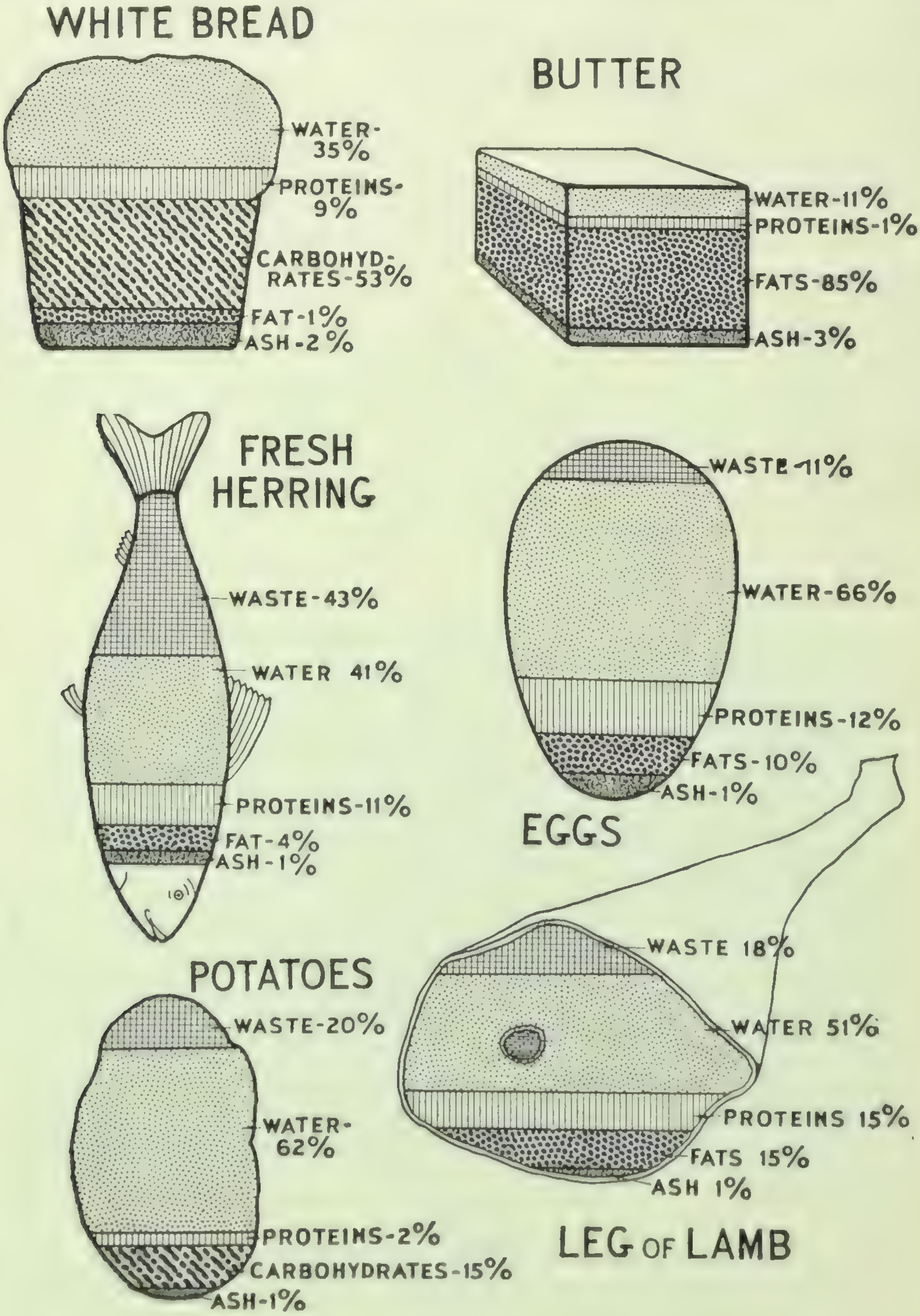


Fig. 212

Diagrams to Show the Various Components of Some Common Foods the minute amount required by the body. In those districts where there is no iodine in the water, goitre is a common ailment. The use of iodized table salt has reduced to a considerable extent the number of goitre cases in those areas.

In addition to calcium, iron and iodine, the following elements appear to be necessary to growth and good health: sodium, potassium, chlorine, fluorine, manganese, magnesium, phosphorus, boron, copper and zinc.

Fruits, vegetables, meat, and common salt usually supply the body with a sufficient quantity and variety of these elements. Scientists have found that these elements are needed in the body for the following purposes:

(1) For proper bone formation.
(2) In the digestive processes.
(3) For the changes which take place in the blood.

(5) VITAMINS. It has been discovered that in addition to carbohydrates, fats, proteins, and mineral salts, there are other materials which, even though required in very small amounts, are essential to life. These substances are called *vitamins*. They are named after the letters of the alphabet and the best known are A, B, C and D. The presence of all in the diet is necessary in order to enjoy good health. Because very few foods contain all the vitamins, it is important to remember that we can only secure a liberal quantity of all the vitamins by eating a variety of foods.

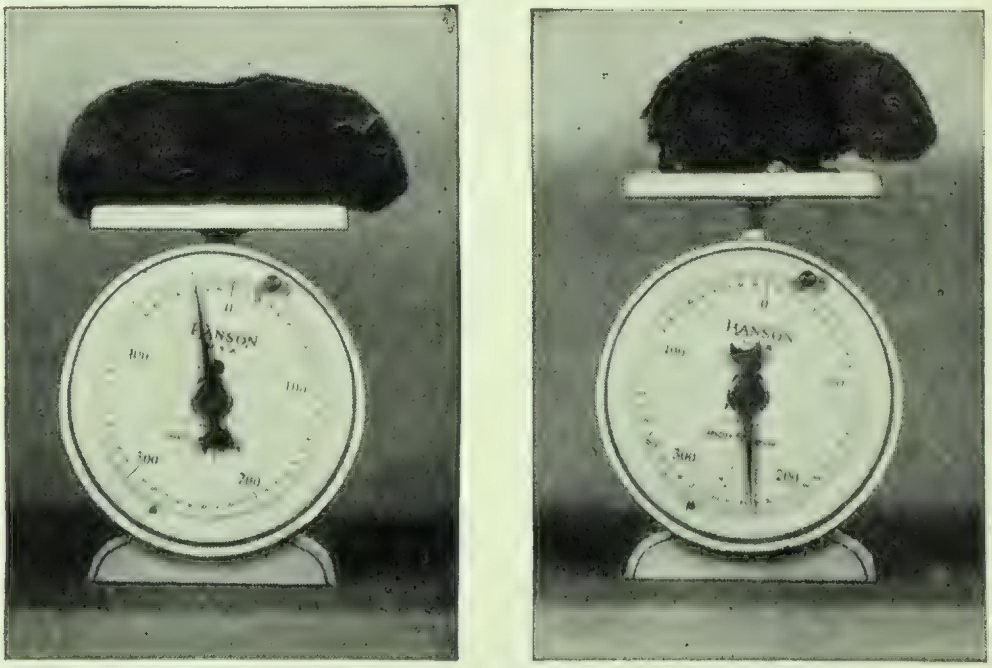
Vitamin A. This is found in large quantities in milk, butter, egg yolk, cod-liver oil, and, to a lesser degree, in beef fat and many vegetable foods, such as lettuce, spinach, cabbage, carrots, and potatoes. In general, it can be said that this vitamin is present in green leaves and in the embryos of many seeds. The presence of this vitamin in the diet builds up the body's resistance to infections of the mucous membranes. The absence of vitamin A in the diet impairs vision and results in severe colds and sore eyes.

Vitamin B Complex. Vitamin B complex includes a number of substances, the most important of which are thiamin chloride, riboflavin and niacin. *Thiamin chloride*, sometimes known as vitamin B_1, occurs in the whole grains of wheat, oats, and barley; in certain vegetables such as peas and beans; and also in livers, kidneys, and yeast. This substance increases the appetite and is beneficial to the digestive and nervous systems. Thus, thiamin chloride is necessary for proper growth and is especially needed by small children. A lack of this substance in the diet for a long time results in the disease known as *beriberi*. Persons suffering from this disease lose control of their muscles and their body wastes away.

Riboflavin, also known as vitamin B_2, occurs in milk, eggs, fresh vegetables, livers, kidneys, and yeast. This vitamin speeds up the transfer of oxygen to the body cells in the process of oxidation. A lack of this substance in the diet causes disorders of the skin and eyes.

Niacin occurs in milk, green vegetables, livers, kidneys, and yeast. This material aids in the proper functioning of the digestive and nervous systems of the body. If it is omitted from the diet for a long period of time, a disease known as *pellagra* attacks the body. Symptoms of this disease are blotches on the skin, intestinal disorder, and nervousness.

Vitamin C. This vitamin occurs in fresh fruits and vegetables, especially in citrus fruits and tomatoes. It assists in the growth of bones and teeth. A lack of vitamin C causes crumbling of the teeth and certain germ infections may develop in the body. The disease known as *scurvy* is due to prolonged lack of this vitamin in the diet. The characteristics of this disease are anemia, hemorrhage and loosening of the teeth. In the days of



Courtesy of Canadian Medical Association

Fig. 213—The Two Guinea-pigs Pictured Above are the Same Age, the Only Difference in Their Diet Being the Amount of Vitamin C. One of Them Weighs 471 Grams, the Other Just 232 Grams

sailing vessels this disease was quite common, and some intelligent sea-captains, such as Captain Cook, made their crews eat daily rations of onions or lemon juice. The famous explorer Jacques Cartier lost many men from scurvy until the Indians showed him how to make a kind of tea brewed from the tops of evergreen trees. Heat and air are great enemies of vitamin C; foods containing this vitamin should be protected as much as possible from these destructive agents.

Vitamin D. This vitamin regulates the absorption of calcium and phosphorus, and so it is essential to the formation of bones and teeth. Lack of this vitamin in the diet of children results in *rickets*, which is characterized by bowlegs, poor teeth and digestive troubles. Vitamin D occurs in fish-liver oils, milk and eggs; it is also produced in the skin by exposure to sunlight.

2. Textiles

A textile can be defined as a substance which has been made by weaving, or which can be woven. Most of the materials which are used for the making of textiles have a fibrous structure, and they are often known as the *textile fibres*. These fibres can be classified into three groups: the vegetable fibres, cotton and linen; the *animal fibres*, wool and silk; and the *artificial fibres*, such as the various types of rayon. Fig. 214 shows how cotton, wool, and silk fibres appear when observed through a microscope. Much money is spent every year by Canadians for textiles and the textile industry is a large and important one.

An examination of Fig. 214 shows that the *cotton* fibre has a twist, which makes it especially good for spinning, because when the fibres are twisted together they interlock and cohere. The twist also gives a certain amount of elasticity to the cotton fibre.

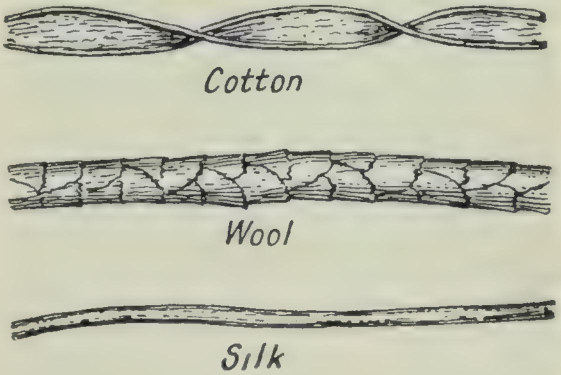

Cotton
Wool
Silk

Fig. 214—Textile Fibres as They Appear Through a Microscope

Wool is the hairy covering or fleece of sheep. There are many varieties, depending upon the type of sheep from which it is obtained. Examination of Fig. 214 shows that wool fibres have an outer coating of flattened cells, which overlap somewhat like the scales of a fish. These scales give to wool a characteristic appearance, when observed under the microscope; thus it can be readily distinguished from other types of fibres.

Linen comes next to cotton in importance as a vegetable fibre. This fibre occurs as a thin layer just under the bark of the stalk of the flax plant. It is quite different in structure and appearance from cotton. The linen fibre is made up of a number of elongated thick-walled cells from one inch to two inches in length. These cells are held together by a sticky material to form a filament from 12 to 36 inches in length.

Since cotton and linen are both composed chiefly of cellulose, their chemical properties are very much the same. Unbleached linen is much stronger than cotton but less elastic.

Silk, unlike cotton, linen and wool, has no cellular structure. The silk worm produces this fibre when it builds its cocoon; making the cocoon takes about three days. The silk worm gives off a viscous silk-liquid into the air through two small openings in its underlip, and this liquid hardens on exposure to the atmosphere. The raw silk is obtained as a continuous thread from the cocoon, varying in length from 300 yards to 1000 yards.

Silk has a very high tensile strength, being about one-third that of a steel wire of the same cross section. It is also a very elastic substance, and a poor conductor of heat and electricity.

Rayon is the name applied to certain artificial fibres, made from wood cellulose or cotton cellulose, which when examined by the naked eye seem to be the same as silk. Examination by means of a microscope, however, shows that such is not the case. Rayon will be considered in the next section of this chapter.

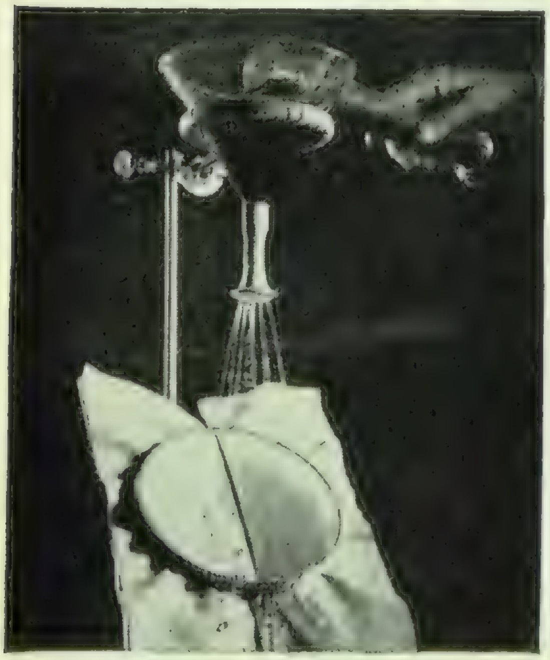


FIG. 215—WATER-REPELLENCY TEST OF A CHEMICALLY TREATED FABRIC AS COMPARED TO AN UNTREATED CLOTH

The burning test is a simple way to tell one kind of textile fibre from another. Cotton and linen both burn easily and give off an odour like that of burning wood or paper. Wool and silk burn slowly and give off an unpleasant odour, like that of burning hair or feathers. The vegetable fibres burn completely and leave a small amount of gray ash. The animal fibres, on the other hand, go out quickly and leave a gummy residue, especially noticeable in wool. Rayon, since it is produced from wood or cotton, burns in the same way as do cotton and linen fibres.

The needs of World War II gave rise to the production of special finishes for use on textiles. These include treatments which give the textile such properties as resistance to water, fire, attack by micro-organisms and chemical warfare agents (poisonous gases).

Textiles can be made water-repellent by various means, such as treatment with wax-solvent mixtures or water-wax emulsions. Such methods do not seem to be as satisfactory as the so called "permanent" types of chemical treatments, such as the *velan* treatment. Fig. 215 shows a comparative water-repellency test of a chemically treated fabric and of untreated cloth.

Courtesy of Courtaulds (Canada) Limited

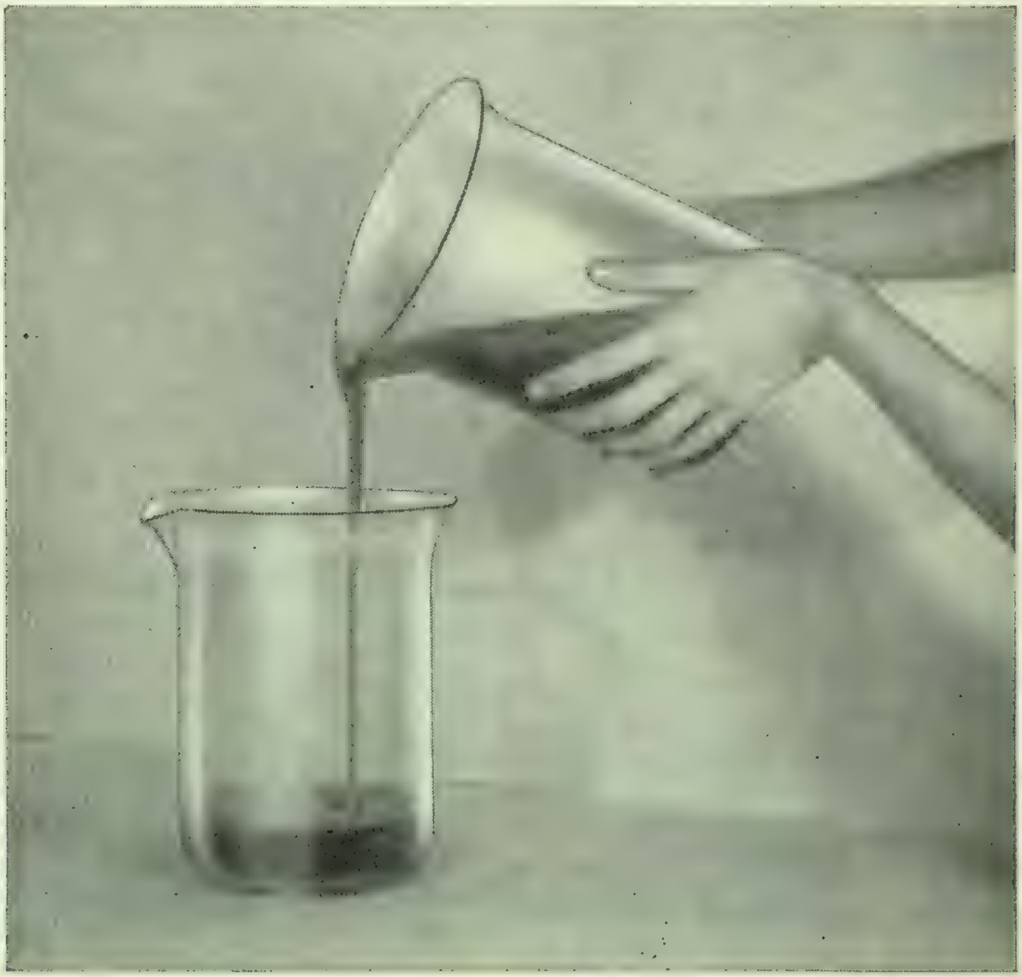
FIG. 216—THESE ARE THE LAPS OF PURE WOOD CELLULOSE FROM WHICH ORDINARY RAYON IS MANUFACTURED

3. Rayon

Rayon, or artificial silk, which has become in recent years a widely used product, resembles good paper in that it consists of pure cellulose. Four different processes have been developed for its manufacture; of these the viscose process is used for over 80 per cent of the world's rayon production.

High grade sulphite wood pulp (usually obtained from spruce trees), is the starting point for the production of artificial silk. Canada supplies almost 40 per cent of the world's requirement of wood for this purpose. The sulphite wood pulp, which consists chiefly of cellulose, is treated for two hours with a weak solution of sodium hydroxide (caustic soda), resulting in the formation of alkali cellulose. Surplus moisture is squeezed out of this alkali cellulose, and the material is then torn to shreds, which are allowed to stand for 24 hours in a closed vessel.

Carbon disulphide is then added to the shredded alkali cellulose and a solution, known as *viscose*, is formed. This solution is allowed to "ripen" for a day or two, after which it is ready for spinning. The viscose is forced through fine holes into a bath of dilute sulphuric acid and sodium bisulphate. The acid solution causes the fine jets of liquid to change into threads which are spun into the material known as rayon.



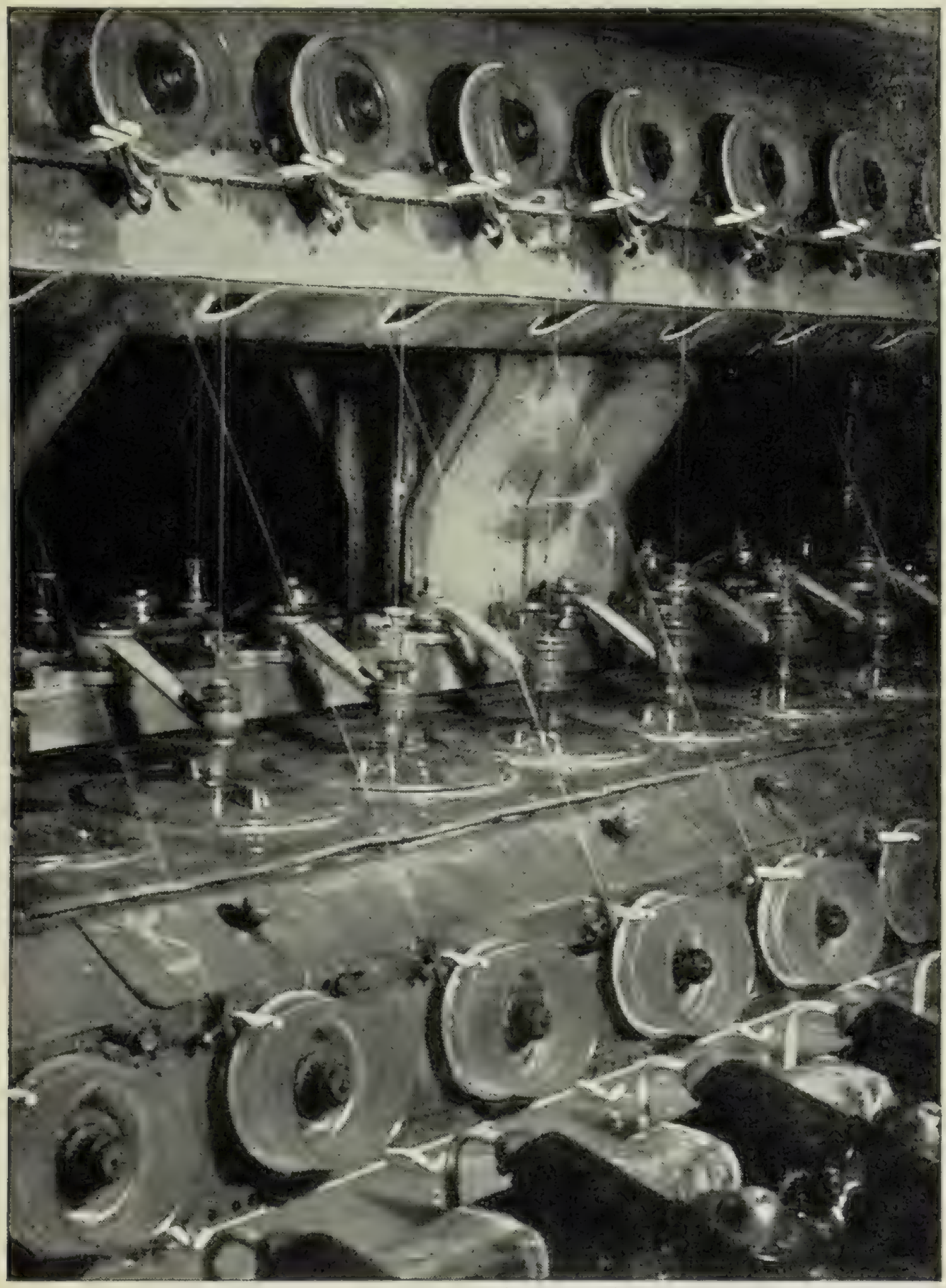
Courtesy of Courtaulds (Canada) Limited

Fig. 217—This is the Thick Viscous Liquid, the Man-made Silk Fluid, From Which the Filaments of Ordinary Type Rayon are Produced

This artificial silk is altogether different from the natural product. It lacks the tensile strength of pure silk but it has a fine appearance, and this, combined with its cheapness, has led to its being used extensively either alone or as a mixture with wool or cotton.

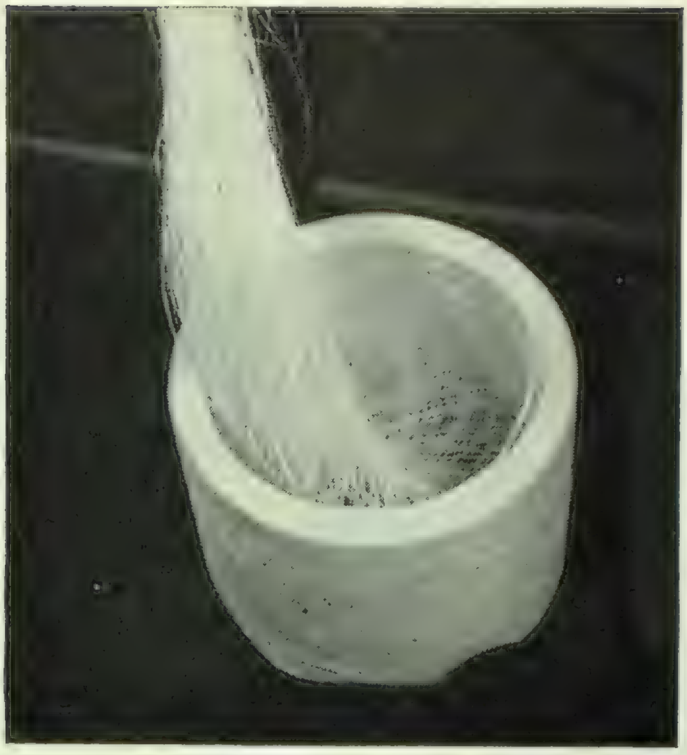
Celanese rayon is another type of artificial silk which is made from spruce cellulose. Its production is quite different from that of viscose. Viscose is a pure cellulose, whereas celanese is *cellulose acetate.* However, the mechanical operation of producing the threads from the liquid is the same.

It is interesting to know that *cellophane*, which is used so much as a protective covering for many articles of commerce, has the same chemical composition as viscose rayon but the cellulose is precipitated as thin sheets and not as threads. "Safety" motion picture films have the same composition as celanese, being made from cellulose acetate.



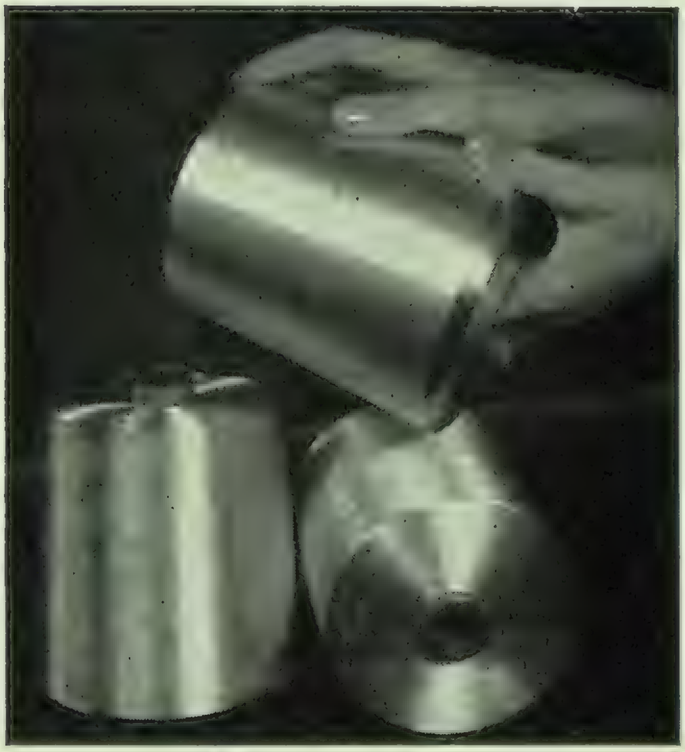
Courtesy of Courtaulds (Canada) Limited

Fig. 218—The Ordinary Type Filaments are Emerging from the Coagulating Bath, Passing Around the Drums, and Being Twisted Into a Coarser Thread. The Funnels Lead the Threads to the Spinning Boxes



Courtesy of Courtaulds (Canada) Limited

FIG. 219—THIS IS THE ORDINARY TYPE RAYON YARN FROM THE SPINNING BOX

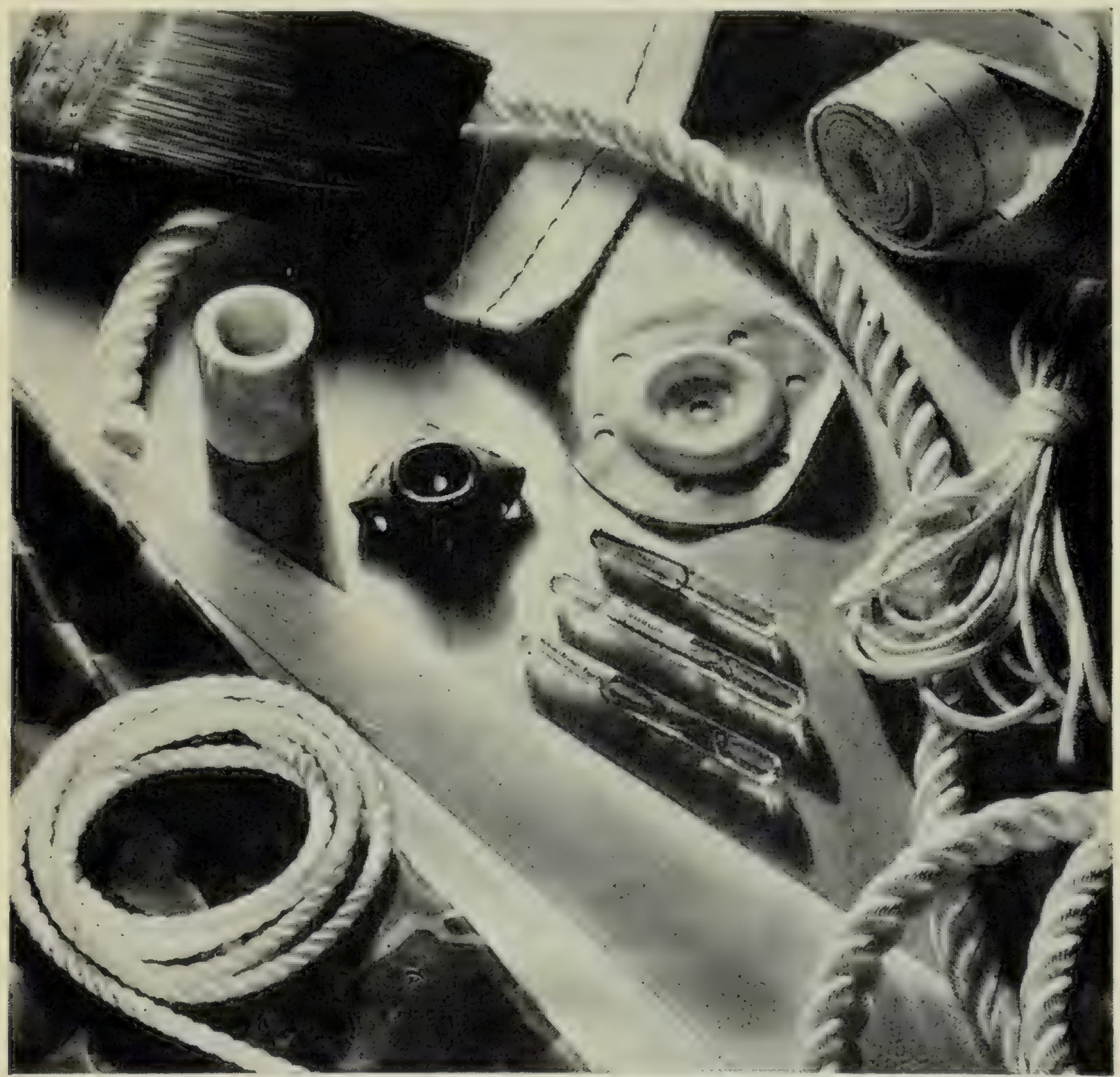


Courtesy of Courtaulds (Canada) Limited

FIG. 220—THIS IS ORDINARY TYPE RAYON READY TO BE PACKED AND SHIPPED TO A TEXTILE MILL WHERE IT WILL BE WOVEN OR KNITTED INTO BEAUTIFUL FABRICS

4. Nylon

Nylon is the name of a new group of chemical compounds discovered about 1929 in the laboratories of the du Pont Company in the United States. The manufacture of nylon is a very complicated chemical process, the details of which can only be understood by chemists. It is said that nylon is derived from coal, air and water, but this is done through an intermediate product, benzene, which is obtained from coal tar. The type of nylon which is used as a textile fibre starts with the production of benzene from coal tar, the production of nitrogen and oxygen



Courtesy of Canadian Industries, Ltd.

FIG. 221—NYLON'S USES HAVE EXPANDED FAR BEYOND HOSIERY AND TOOTHBRUSH BRISTLE. SHOWN HERE ARE NEW NYLON PRODUCTS: ARRANGED CLOCKWISE, BEGINNING WITH THE PAINT BRUSH WITH TAPERED NYLON BRISTLE, ARE PARACHUTE HARNESS WEBBING, PARACHUTE SHROUD LINES, HEAVY NYLON ROPE, PARACHUTE CLOTH AND LIGHT NYLON ROPE. CENTRED, LEFT TO RIGHT, ARE NYLON PLASTIC BEARING, CARBURETTOR DIAPHRAGMS OF NYLON FABRIC, AND SURGICAL SUTURES

from the air and the production of hydrogen from water. These substances are combined together in certain complicated chemical processes and the result is nylon flake.

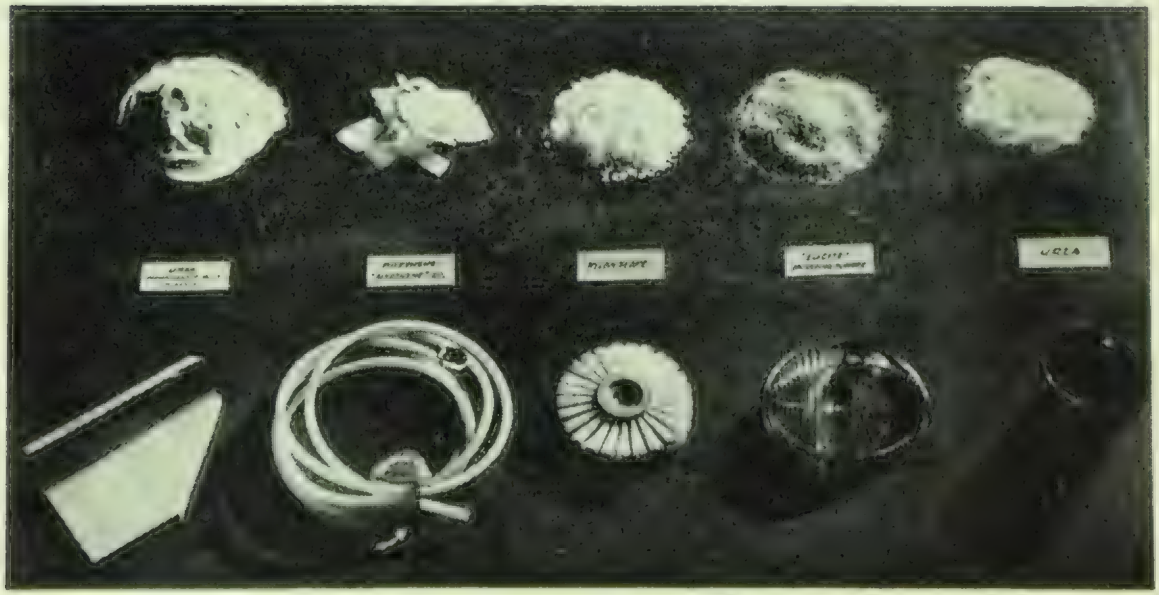
The nylon flake is melted under pressure to a thick, gummy mass. This viscous substance is forced through small holes in a metal disc known as a spinneret. It comes out in fine filaments which harden in cold air. These tiny filaments are gathered together to form a strand of yarn and, after a certain mechanical treatment, it is woven into a cloth which is somewhat like silk in composition and properties.

Nylon is said to be stronger and more elastic than silk, wool, or cotton. It is used in making hosiery, brush bristles, nylon rope, bearings, surgical sutures and many other articles of commerce which were formerly manufactured from silk. Fig. 221 shows a few of the uses of nylon.

5. Plastics

Bakelite and other formaldehyde types of plastics have already been considered (see page 403). Plastics can be defined as a large group of natural and synthetic organic materials, derived from cellulose, proteins, hydrocarbons or resins, which are moulded (under heat and pressure), extruded, cast or fabricated into various shapes.

Moulded plastics are classified into two types, *thermosetting* and *thermoplastic.* A thermosetting plastic is one that "sets" on the application of heat. Many of the plastic materials in use



Courtesy of Canadian Industries, Ltd.

FIG. 222—SAMPLES OF PLASTIC MOULDING POWDERS AND TYPICAL PRODUCTS IN WHICH THEY ARE USED

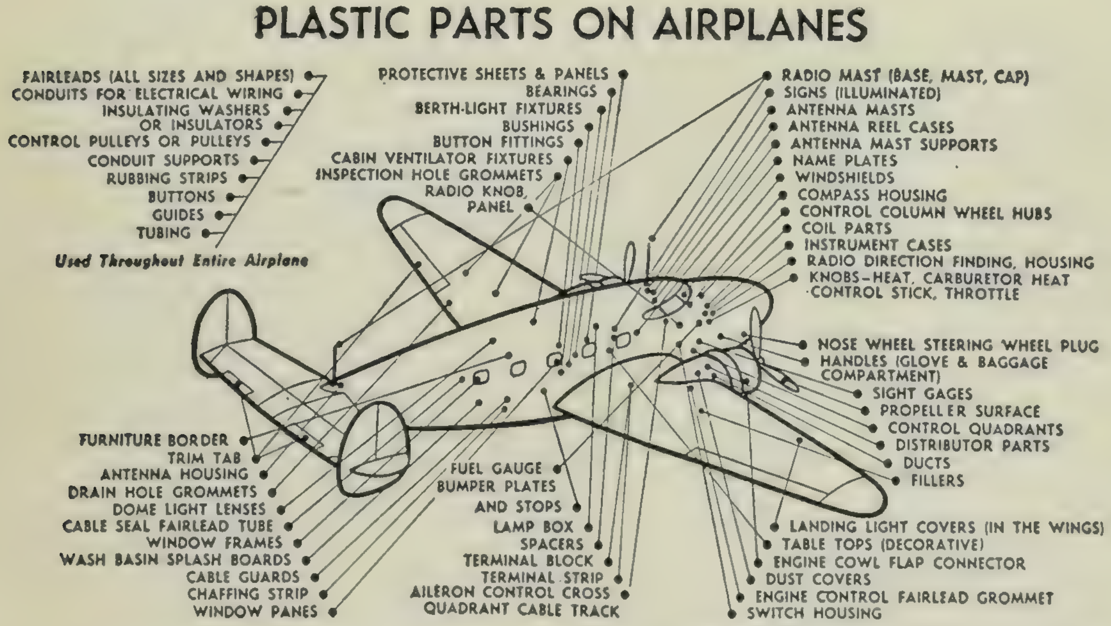
today, headed by the phenol formaldehyde and urea formaldehyde plastics, are of the thermosetting type. These do not soften much when reheated and cannot be remelted. A thermoplastic can be softened by reheating and can be remelted. Thus, this type can be remoulded indefinitely. The cellulose and vinyl plastics are important members of this type.

Phenol formaldehyde was the first thermosetting material to be used extensively in industry. It is used in the production of a very wide variety of articles having both domestic and industrial applications. It is commonly seen in telephone hand sets, black and brown bottle caps, pot handles, etc. Some trade names used for it are *Bakelite*, *Durez* and *Resinox*.

Urea and melamine formaldehyde plastics are also thermosetting and they are used to make articles such as coloured bottle caps, buttons, clock cases, plastic dinnerware, etc. Some of its trade names are *Plaskon*, *Beetle* and *Melmac*.

Methyl methacrylate is a thermoplastic acrylic resin. It is generally seen in clear, glass-like form and was used during World War II in aircraft cockpit and gun turret enclosures. This plastic has the unique property of "piping" light, and is widely used in surgical and dental instruments. Trade names for it are *Lucite*, *Perspex* and *Plexiglas*.

Cellulose plastics are all based on natural cellulose, whose molecules have been changed to give a wide variety of properties. For example, when cellulose is treated in a certain



Courtesy of Canadian Industries ,Ltd.

Fig. 223—A Diagram to Show That Many Parts of Airplanes are Made From Plastics

way with nitric acid, cellulose nitrate is produced. This is known commercially as *Pyralin*, *Celluloid* and *Nitron*. *Cellulose acetate* is another example of this type of thermoplastic. It is sold under the trade name of *Plastacele*.

Other thermoplastics include the polystyrenes, the vinyls, the polyethylenes and the nylons.

Much progress has been made in this field in a comparatively short time. Several hundred plastics can now be obtained commercially in at least 20 different types and new plastics are being developed every year. Some people have the impression that plastics will soon replace glass, wood, porcelain, rubber and even metal. This impression, is, of course, a mistaken one. While plastics have been responsible for many new articles and have replaced some of the older materials for certain uses, the day has not yet come when plastics can replace entirely the older materials used for building or for manufacturing.

6. Natural Rubber

The material known as "rubber" is the basic ingredient of a very great variety of articles of commerce, and is one of the most necessary and useful materials in modern civilization. Rubber was known to the natives of South America and the West Indies at the time of the first European explorations. The term "caoutchouc," which is applied to unvulcanized rubber, is derived from a word in one of the Indian dialects which means "weeping tree." The word "rubber" was introduced into common use in the English language in 1770 by Priestley, since he found that it was being used by draftsmen to rub out graphite marks on paper.

The sensitiveness of rubber to heat limited its use in waterproofed fabrics to climates which are mild the year around. In winter unvulcanized rubber is hard and brittle, whereas in summer it is soft and sticky. The present rubber industry really began in 1839 when Charles Goodyear, a New England inventor, found that heating rubber with sulphur would greatly change the properties of the resulting product, which was not changed by the cold of winter or the heat of summer. This process of heating rubber with sulphur is known as *vulcanization*.

The first chemical analysis of rubber was made by the great English experimenter, Michael Faraday, who found that its simplest formula is C_5H_8. Thus, rubber is a hydrocarbon. It has been found, however, that rubber is a liquid having a molecular weight many times that represented by the formula C_5H_8. It is what the organic chemist calls a *polymer.* Polymers can be compared to chains of paper clips, where each paper clip would correspond to a molecule, called a *monomer* when independent but called a polymer in the chain. The chain-forming process is called *polymerization.* The number of C_5H_8 monomers which have to be chained together to form a polymer is still uncertain. The minimum seems to be 200, the maximum 4000. The longer the hydrocarbon chain is, the better the quality of the rubber. The formula for natural rubber is usually shown as $(C_5H_8)_X$, where x represents the number of monomers in this polymer.

Natural rubber at 20° C. is tough and highly elastic, but the temperature range over which it keeps these desirable properties is very narrow. If chilled to 10° C. it becomes stiff, and with severe cooling it changes to quite a brittle material. If heated above 25° C. it becomes sticky and loses its elasticity. This sensitiveness to temperature changes makes raw rubber almost worthless for most uses. If rubber is thoroughly mixed with sulphur and heated, a change in its properties takes place so that its sensitiveness to heat is greatly lessened. If the amount of sulphur is small, that is five per cent or less, the rubber remains tough and elastic, and it retains these properties over a range of from —30° C. to 150° C. If the amount of sulphur is increased until it makes up from 25 to 30 per cent of the mixture, a hard product is obtained after vulcanization. The chief difference between raw rubber and the soft vulcanized rubbers, containing not more than five per cent sulphur, is that the vulcanized rubber, when stretched, returns to its original shape and dimensions, and raw rubber does not. Any process producing this change in sensitiveness to heat and cold is known as "vulcanization," and because of it rubber is a most important commercial material. As a rule, the addition of sulphur is involved in these processes.

Natural rubber occurs as a suspension of very small particles (colloidal) in the white, milk-like fluid, called "latex," which is found in the leaves, bark, and roots of a large variety of trees, shrubs, and vines. Nearly all the natural rubber of commerce comes from a tree, *Hevea brasiliensis*, which is found in the Amazon Valley. Since 1876 this tree has been cultivated on the great plantations which are scattered throughout the tropics in the Far East and certain parts of tropical Asia, Africa, and the Americas. These plantations cover an area of about 9,000,000 acres, and produce about 1,000,000 long tons of rubber per year. In normal times about half of the total world production is sold to the United States, the price being around 20 cents per pound.

The uses of articles or materials of which rubber is the chief component are very numerous. A few common and outstanding uses of rubber are: automobile tires, footwear, fabrics, thread, insulation of copper or aluminum wire, coating of metals, hard rubber for storage battery cases, fire hose, belting for machines, washers, gaskets, golf balls, hot-water bags, bathing caps, toys and gloves.

7. Synthetic Rubbers

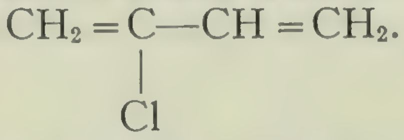
The various synthetic rubbers or *elastomers* ("elastic parts") produced in commerce are quite different in their chemical composition. A few of them are made from two separate starting materials which are polymerized in the same operation to form mixed polymers or *copolymers*. In these copolymers the two substances are chemically combined in the polymeric chain. The unsaturated hydrocarbon, butadiene, $CH_2=CH—CH=CH_2$, is, as a rule, one of the starting substances. At the present time, the other two materials used in industry are styrene, $C_6H_5—CH=CH_2$, and acrylonitrile, $CH_2=CH—CN$. Butadiene and styrene produce a synthetic rubber known as *Buna S*. Butadiene and acrylonitrile form products known as *Perbunan* or *Perbunan extra*, depending on the amount of acrylonitrile used. Butadiene is also used in the production of *Ameripol*, *Hycar*, and *Chemigum*, the other starting materials being trade secrets at present. That polymer, consisting chiefly of isobutylene, $(CH_3)_2C=CH_2$, is known as *Butyl rubber*.

Buna S is used for tire treads because it shows very good resistance to abrasion. Chemigum, Hycar, and Ameripol also show excellent resistance to abrasion, and so they are also used for tire treads. Polymer Corporation, a company owned by the Dominion Government, situated at Sarnia, Ontario, produces chiefly Buna S, and a relatively small amount of Butyl rubber.

The synthetic rubber, known as *Thiokol*, is formed when ethylene dichloride, $Cl—CH_2—CH_2—Cl$, reacts with sodium polysulphide, Na_2S_X. Thiokol is the outstanding synthetic rubber for resistance to swelling in oils and fats. It is used in the manufacture of hoses, gaskets, etc., for the oil industry.

Natural rubber cannot be used in such articles because it swells rapidly and loses its tensile strength when exposed to gasoline or oil.

NEOPRENE was introduced by the du Pont Company in 1931 and has been used considerably since that time for certain purposes. It is made from products derived essentially from coal, limestone and salt. Coke and limestone furnish calcium carbide, which reacts with water to produce acetylene. Acetylene, in the presence of a catalyst (copper salts), polymerizes to mono-vinyl acetylene, $H—C \equiv C—CH = CH_2$, which reacts with HCl (made from NaCl) to form chloroprene,



$$CH_2 = \underset{\substack{| \\ Cl}}{C} — CH = CH_2.$$

Liquid chloroprene polymerizes to a solid and the resultant product is crude neoprene. It is superior to natural rubber in that it does not swell up when in contact with organic liquids. Due to this property, it is used in gaskets, hose, and other articles which come in contact with petroleum products. For a number of years special tires have been made from neoprene and used in the oil fields with success. Electrical wires and cables are covered with neoprene to protect them from the effects of oils, chemicals, heat, sunlight and the ozone formed around high tension conductors. Neoprene gloves and aprons for workers and chemists furnish protection against solvents, acids and other corrosive chemicals. These are only a few of the many important uses of this important synthetic rubber.

8. Dyes

Recently a silk manufacturer displayed 86 different shades of the colour green, showing to what perfection the art of dyeing has been brought. Thought to have originated in India many centuries ago, dyeing was at first confined to the production of just three colours, red, obtained from the madder plant; blue, from indigo; and purple, from a tiny shellfish, murex. In the city of Florence, Italy, a method of preparing purple dye from certain lichens was discovered in the thirteenth century, and in 1472 the first dye company was started in London, England. It was not, however, until the eighteenth century, when scientists became interested in the perfection of dyeing processes, that the industry became the important one that it is today.

Coal-tar products were introduced into the process in 1856 by a young British chemist, William Henry Perkins. Perkins was working with aniline, a substance obtained from coal tar, in an effort to find quinine. Instead, he discovered amazing colouring properties of certain aniline compounds, which led to a broader field, revealing dye properties in a large number of coal-tar products. His work, which resulted in cheaper and more versatile dyes, brought him a fortune and a knighthood, while industry was given an important use for coal-tar, which had hitherto been considered useless.

Organic chemists have made many synthetic dyes, which are better than those found in nature, because of their much greater variety and adaptability, qualities which are being continually further improved in research laboratories.

9. Organic Insecticides

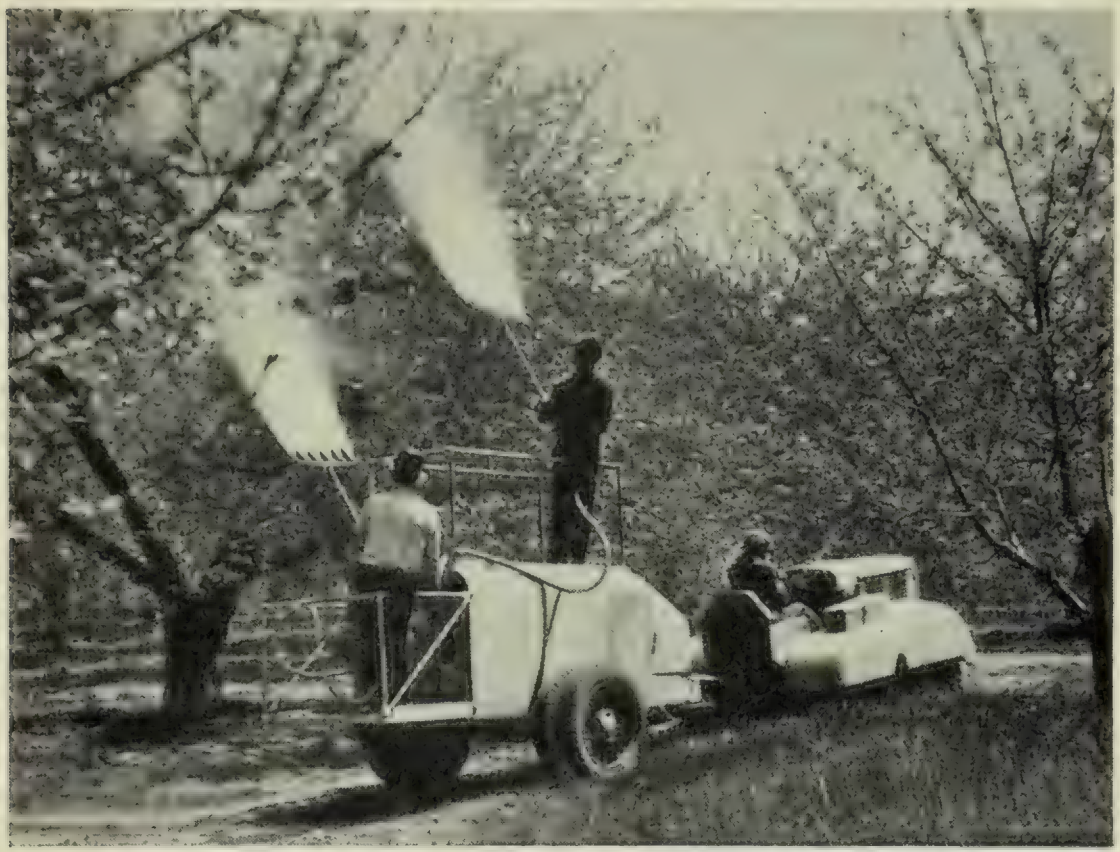
Insecticides are classified into *poison sprays* or *stomach poisons*, and *contact poisons*. The former cause death to insects when taken internally, while the latter bring about destruction of life by mere contact. *Pyrethrum* belongs to the contact class of insecticides.

PYRETHRUM is a flower, somewhat like our ordinary field daisy; it is widely cultivated in Japan. Its blossoms, compressed and packed in bales, are shipped to all parts of the world to be used in the manufacture of insect powder, which is used chiefly in the home.

NICOTINE, a complex compound found in tobacco, is rapid and effective in the destruction of insects. It is generally used as the sulphate, being a contact insecticide, which will give control over such insects as aphis, thrips, leaf hoppers, and similar sucking insects. Nicotine sulphate kills not only by contact but also by the nicotine fumes which are given off.

Early in World War II, hordes of disease carrying insects hampered our armies in the field and filled our base hospitals with casualties due to these insect enemies. In addition, our food production on the home front was reduced by a large number of other insect pests. Scientists attacked this problem with great vigour, and in a short time a number of new chemicals were available to aid in the war against insects.

One of the most important of these new chemicals is D.D.T. (dichloro-diphenyl-trichloroethane). D.D.T. is a white, odourless powder, insoluble in water but quite soluble in acetone or alcohol. It is a contact poison like nicotine. This insecticide first stimulates the insect's activity, then paralyzes its nervous system and finally causes death. D.D.T. is readily manufactured from common chemicals. It provides protection for a month against body lice when dusted on clothing, even if laundered every week, and against flies for four months after it is sprayed on walls. D.D.T. is very potent against many species of insects.



Courtesy of Canadian Industries, Ltd.

FIG. 224—ORCHARD SPRAYING FOR PEST CONTROL SHOWS HOW FARMER AND CHEMIST WORK TOGETHER TO PREVENT CROP DESTRUCTION

It has already been shown that it destroys bedbugs, lice, roaches, Japanese beetles, European corn borer, oriental fruit moth, certain leaf hoppers, ticks and fleas. This new chemical has been given the credit for having saved Sicily and Italy during World War II from an epidemic of typhus, when more than 2,000,000 persons were dusted with it to kill disease-carrying body lice.

10. Perfumes

Perfumes have been used from earliest times. There is no record of ancient periods which does not mention the use of fumes or volatile substances in one form or another. A desirable perfume is a blend or combination of several compounds, possessing an odour, which are mixed in such a way as to produce a single pleasant smell. Often these perfumes consist of at least a dozen ingredients all selected to give the desired effect. For example, in *lavender water* musk and civet are used. Of course, these scents are in a very dilute form when used as perfumes.

Three substances, musk, civet, and ambergris, are most essential for the production of fine perfumes. These materials are of animal origin and they are used in perfume mixtures as tincture, giving not only a certain odour, but at the same time acting as fixatives. A fixative helps to hold the delicate odours of the perfume for a long time. Ambergris is a vile-smelling substance produced by whales, and, at times, it is found floating on the ocean and cast upon the seashore. However, most of it is secured by whalers and brought back in whaling boats. It comes in black or gray lumps of varying sizes and weights, and sells for a high price due to the fine odour it gives to perfumes. Musk is obtained from the male musk deer. Civet comes from the civet cat, found in Abyssinia.

Pure phenol, known also as carbolic acid, C_6H_5OH, has a most disagreeable smell. Phenol can be readily changed into salicylic acid, $C_6H_4(OH)COOH$, which when heated with methyl alcohol and sulphuric acid, gives the ester, methyl salicylate, $C_6H_4(OH)COOCH_3$. Methyl salicylate is the chief component of *oil of wintergreen.*

Oils of jasmine, orange blossoms, heliotrope, tuberose and many others are made from coal-tar products. Most of these coal-tar products, which serve as starting points for perfumes, possess an evil odour. However, the organic chemist can convert these compounds to others, which when blended with ambergris, musk or civet, give excellent perfumes.

EXERCISES

1. (a) What are the chief functions of foods?
   (b) What are the chief classes of foods?
2. (a) What carbohydrates are used as foods?
   (b) What is the chief purpose of a carbohydrate in the diet?
3. (a) What is a fat?
   (b) In what common foods do fats occur?
   (c) What is the function of a fat in the diet?
4. (a) What is a protein?
   (b) What is an amino acid? Write the structural formula for glycine.
   (c) Name five foods which contain proteins.

5. (a) What is meant by the mineral salts of foods?
   (b) Write short notes on the importance of the following elements in the diet: calcium, iron, and iodine.

6. (a) What is a vitamin?
   (b) Write short notes on the following vitamins: A, B, C and D.

7. (a) What is a textile?
   (b) Write short notes on cotton, linen, wool and silk.
   (c) Describe what takes place when each of the common textiles is placed in a flame.

8. (a) Write a short note on the viscose process for the manufacture of rayon.
   (b) What is celanese rayon?
   (c) What is cellophane?

9. (a) What is nylon?
   (b) Write a short note on the production of nylon.
   (c) Tabulate five uses of nylon.

10. (a) What is a plastic?
    (b) What are two chief types of plastics? Define each and give one example of each type.

11. (a) What is natural rubber?
    (b) Why is it unsuitable for commercial use?
    (c) Who discovered the vulcanization of rubber? Why is this process so important?

12. (a) What is a polymer?
    (b) What is a monomer?
    (c) What is polymerization?
    (d) Is natural rubber a polymer? Explain.

13. (a) Discuss the effect of temperature changes on the properties of native rubber.
    (b) Discuss the effect of blending sulphur with natural rubber.

14. Tabulate ten uses of rubber.

15. (a) Many synthetic rubbers are said to be copolymers. Discuss this statement briefly.
    (b) Name three synthetic rubbers used in the manufacture of automobile tires.
    (c) What is thiokol and what is an outstanding property of this type of synthetic rubber?
    (d) Write a note on neoprene.

16. Write brief notes on the following: (1) coal-tar; (2) insecticides; (3) perfumes.

CHAPTER LII

THE PERIODIC SYSTEM

1. Early Attempts at Classification

Since scientists are always anxious to classify facts, chemists have made many attempts to classify the chemical elements. One of the first attempts to classify the elements was the division into metals and non-metals. The metals were defined as elements whose oxides combine with water to form bases. Non-metals, on the other hand, formed oxides which combine with water to form acids. This classification is not an accurate one because several of the elements, depending upon the conditions, act as either metals or non-metals. For example, zinc burns in air to form zinc oxide, ZnO, which reacts with water to produce a base, zinc hydroxide, $Zn(OH)_2$.

$$2\ Zn + O_2 \longrightarrow 2\ ZnO$$
$$ZnO + H_2O \longrightarrow Zn(OH)_2$$

Zinc hydroxide behaves as a normal base by reacting with a strong acid, such as hydrochloric acid, to form the salt, zinc chloride, $ZnCl_2$.

$$Zn(OH)_2 + 2\ HCl \longrightarrow ZnCl_2 + 2\ H_2O$$

However, zinc hydroxide, in the presence of a strong base, such as sodium hydroxide, ionizes as an acid, and forms a sodium salt with the sodium hydroxide.

$$Zn(OH)_2 \rightleftharpoons H_2ZnO_2 \rightleftharpoons 2\ H^+ + ZnO_2^{--}$$
$$H_2ZnO_2 + 2\ NaOH \longrightarrow \underset{\substack{\text{sodium}\\ \text{zincate}\\ \text{(soluble in water)}}}{Na_2ZnO_2} + 2\ H_2O$$

Elements, such as zinc, which behave either as metals or non-metals, are known as *metalloids* or *amphoteric* elements.

The first indication of a significant relationship between the atomic weights and the properties of the elements was discovered by Döbereiner, the German chemist, in 1829. He pointed out that there were certain elements, quite similar in physical and chemical properties, which could be grouped into sets of three (triads). He showed that the central element in these groups was intermediate in properties between the other two members of a triad. Furthermore, the atomic weight of the central element was the approximate arithmetical mean of the other two. The following triads illustrate this relation:

Element	**Atomic Weight**	**Mean**
Chlorine	35.46	81.19
Bromine	79.92	
Iodine	126.91	
Sulphur	32.06	79.84
Selenium	78.96	
Tellurium	127.61	
Calcium	40.08	88.72
Strontium	87.63	
Barium	137.36	

The relationships discovered by Döbereiner were incomplete but they pointed the way to our present periodic system.

The next scientist who contributed in an important way to the problem of the classification of the elements, was Newlands, an English chemist. In 1865 he published a paper in which he described the "Law of Octaves." He discovered that if he arranged the elements in the order of their atomic weights, they grouped themselves naturally in series of seven (octaves), the corresponding elements in each series having somewhat similar properties. The following is a rearrangement of a part of Newlands' original table:

H(1)	Li(2)	Be(3)	B(4)	C(5)	N(6)	O(7)
F(8)	Na(9)	Mg(10)	Al(11)	Si(12)	P(13)	S(14)
Cl(15)	K(16)	Ca(17)	Cr(19)	Ti(18)	Mn(20)	Fe(21)

An examination of the above table shows that the elements placed in a vertical position resemble each other very much in physical and chemical properties. For example, lithium, sodium and potassium show quite similar reactions. Newlands' idea had certain flaws in it, but it will be observed that each time we go through a cycle of seven elements there is, as a rule, a return of somewhat similar properties. For example, starting with lithium, we go through a cycle of seven elements and come to sodium, which is situated right under lithium in the table. If we continue on from sodium, we go through another cycle of seven and come to potassium, which is very similar in its chemical reactions to sodium and lithium. Of course, there are some exceptions in his table. For example, hydrogen is not like fluorine, manganese is not like phosphorus, and iron is certainly not like sulphur. However, Newlands' idea was a great contribution to the classification of the elements and suggested a great chemical law.

Newlands presented his ideas in a paper given before the Chemical Society (London) in 1866, and many of those who heard him took his important idea as a joke. One member even asked him if he "had ever examined the elements according to the order of their initial letters." The society refused to publish his paper in their journal, and it appeared that his ideas were too advanced for the chemists of his day.

2. The Periodic System of Mendeléeff

A few years later, in 1869, a more satisfactory system of classification of the elements was put forward by the Russian chemist, Mendeléeff. At the same time, Lothar Meyer, a German chemist, working independently of Mendeléeff, developed the same system of classification of the elements on the basis of their atomic weights. Books on the history of chemistry give both Mendeléeff and Meyer credit for discovering the important chemical law. However, the name of Mendeléeff is usually associated with the periodic classification of the elements.

FIG. 225—DIMITRI IVANOWITCH MENDELÉEFF (1834-1907). MENDELÉEFF WAS A GREAT RUSSIAN CHEMIST WHO BECAME FAMOUS FOR HIS PERIODIC CLASSIFICATION OF THE ELEMENTS AND FOR HIS PROPOSAL OF THE PERIODIC LAW

Since the days of Mendeléeff and Meyer the system which they developed has been expanded to a considerable extent because of the discovery of new elements, such as the group of inert gases found in the atmosphere. In other ways, too, it has been revised, but the present form of the Periodic Table does not differ very much from that devised by Mendeléeff, and so it is usually referred to as *Mendeléeff's Table of the Elements.* This table is found on the inside back cover of this book and should be examined carefully as you study this chapter.

A careful examination of the modern periodic table brings out some interesting relationships and a few of these are discussed below.

(1) The elements are arranged in *ascending order* of their atomic weights. This is similar to Newlands' table.

(2) The system starts with helium rather than with hydrogen. Hydrogen does not appear to fit into the system at all. It has a valence of *one*, which should place it in Group I. However, the properties of hydrogen are not like those of lithium, sodium and potassium, and so it should not be placed in the same group as those elements. Hydrogen has an atomic weight of 1.008 and an atomic number of one. It is placed by itself, and serves as a kind of measuring stick with which to compare the other elements.

(3) The following elements, arranged in ascending order of atomic weights, make up the first two horizontal rows, which are known as *short periods*. The approximate atomic weight of each element is placed in a bracket underneath the symbol of the element.

He	Li	Be	B	C	N	O	F
(4)	(7)	(9)	(11)	(12)	(14)	(16)	(19)
Ne	Na	Mg	Al	Si	P	S	Cl
(20)	(23)	(24)	(27)	(28)	(31)	(32)	(35.5)

As we go from left to right, the elements change to a marked extent in their properties. For example, lithium is a metallic element, forming a strong base with water. Fluorine, on the other hand, is the most non-metallic element known, forming hydrofluoric acid when combined with hydrogen. However, when we reach neon, we find that it is very similar to helium in properties; so neon is placed directly underneath helium. Sodium is located under lithium for the same reason, and so on until chlorine is reached.

(4) Argon marks the beginning of another horizontal row. As we examine this series, we observe that the similarity in properties is very marked. Argon is like neon, potassium is like sodium, calcium is like magnesium, and so forth. However, as we near the end of this row, we find that the similarity disappears. For example, there is very little resemblance between manganese and chlorine. The next element after manganese is not an inert gas—it is iron, which is one of a series of three elements, nickel and cobalt being the other two. These three

metals make up what is known as a transition group; they serve as a bridge between the row ending with manganese and the one starting with copper. Copper is certainly not like argon, and it cannot be placed under that element. Copper is, therefore, placed in Group I along with other metallic elements, such as silver and gold. When we study this second series, we observe that the similarities between the element under consideration and the element just above it, become more marked. Finally, when we reach bromine, the similarity is very noticeable again. This group of elements, from argon to bromine, is known as the third period. It contains 18 elements and is known as a *long period.* The fourth and fifth periods are also known as double or long periods.

(5) It is observed that between barium and hafnium there is a gap of over 40 units in the atomic weights. This gap contains the so-called *rare earth elements.* The atomic weights and atomic numbers of these elements place them in that position in the table, but their properties very definitely exclude them from being spread out in the chart between barium and hafnium. This is one of the unsolved problems of the periodic classification of the elements.

(6) The diagonal line across the table divides the elements approximately into metals and non-metals. As a rule, the greater the perpendicular distance of an element from this line, the more pronounced are its basic properties if it is a metal, or its acidic properties if it is a non-metal. Thus, fluorine is the most non-metallic element known, and cesium is the most metallic element known.

3. The Periodic Law

The most fundamental principle of the periodic system is the fact that *the properties of the elements, both physical and chemical, are periodic functions of their atomic weights.* This statement is known as the *Periodic Law* and it is one of the important laws of chemistry. The word periodic means recurring at regular intervals. The term function is used here as it is in mathematics. That is, the properties of the elements depend upon their atomic weights. Perhaps the best way to explain the Periodic Law is to take some important properties of elements and show that they are periodic functions of their atomic weights.

Valence is an important property of an element and the most characteristic valence of the elements of each group is shown at the top of the table. The positive valences are indicated by formulas, such as R_2O, RO, R_2O_3, etc. The negative valences, on the other hand, are given by the formulas RH_4, RH_3, RH_2 and RH. The elements of the zero group form no compounds, and so they possess no valence. The lone symbol R shows this, where R represents the elements of that group. It will be observed that the chief positive valence is, in each case, the same as the number of the group. Thus, in Group I it is one, in Group II it is two, etc., up to Group VIII, where the positive valence is eight. Commencing with Group IV, the elements show a negative valence. In Group IV the negative valence is the same as the positive valence, but from there on it decreases regularly until Group VIII is reached; there the negative valence becomes zero.

The formulas of a few typical compounds are shown in Table 29 to bring out the periodic gradation of positive and negative valence. From a study of this table it would appear that this property of valence is a periodic function of the atomic weights of the elements under consideration.

TABLE 29—THE FORMULAS OF SOME TYPICAL COMPOUNDS

Group	0	1	2	3	4	5	6	7	8
Positive Valence		Li_2O K_2O	BeO MgO	B_2O_3 Al_2O_3	CO_2 SiO_2	N_2O_5 P_2O_5	SO_3 CrO_3	Cl_2O_7	OsO_4 RuO_4
Negative Valence					CH_4 SiH_4	NH_3 PH_3	H_2O H_2S	HCl HBr	

The acid and base forming properties of the elements are also a periodic function of the atomic weights. The elements in Group I are strongly base forming. For example, sodium hydroxide, $NaOH$, and potassium hydroxide, KOH, are strong bases. The elements in Group II are also distinctly base forming elements, but they are not as strong as the bases formed by the elements of Group I. For example, calcium hydroxide, $Ca(OH)_2$, and magnesium hydroxide, $Mg(OH)_2$, are not as strong as $NaOH$ or KOH. The elements of Group III are amphoteric, forming both acids and bases. However, the elements of this group are more strongly basic than acidic in their properties. The elements of Group IV are also amphoteric. For example, tin forms salts, such as stannic chloride, $SnCl_4$.

It also forms acids, such as meta-stannic acid, H_2SnO_3. The elements of Group V are distinctly acid forming and this property predominates. Thus, nitric acid, HNO_3, and phosphoric acid, H_3PO_4, are produced from nitrogen and phosphorus, two typical elements of Group V. The elements of Group VI are almost entirely acidic in nature, forming strong acids, such as sulphuric acid. In Group VII we find no basic properties at all, except in manganese. This element belongs to the first series of a double period and shows practically no group correspondence.

4. Relations Inside the Groups

Within any one group we observe a gradual change of physical and chemical properties from the top to the bottom. For example, in Group I the metallic properties of the elements become more pronounced as the atomic weight increases. Thus, cesium, at the bottom of Group I, is the most active metal in this group. The changes in a group are not as sharp as the changes in a series, where the elements change from very active metals to non-metals. In any group the valences of the elements are the same or nearly so. An examination of any group in the table shows that the first two members are typical elements of the group. After these two, we observe that the elements are placed to the left or to the right side of the group. Those on the left are said to make up *sub-group A*, and those on the right, *sub-group B*. Thus, lithium and sodium are the typical members or "pace setters" of Group I; potassium, rubidium and cesium make up sub-group A, and copper, silver and gold make up sub-group B.

5. The Advantages of the Periodic System

(1) This system has given chemists a satisfactory classification of the elements, and it has greatly simplified the study of the elements.

(2) It made possible the prediction of new elements. At the time Mendeléeff made up his table, there were a number of spaces between the elements. He explained that these blank spaces were for the elements which had not yet been discovered. Mendeléeff was bold enough to predict the discovery of several new elements, and, on the basis of their location in the table, foretold their properties. A few years later when these elements were discovered, their predicted and actual properties were

almost exactly the same. Three of these elements were gallium, germanium, and scandium.

(3) It suggested errors in the atomic weights used at the time that Mendeléeff proposed his table. There were certain elements which did not fall into the groups into which their properties placed them. In such cases Mendeléeff claimed that the atomic weight was incorrect. For example, cesium at that time was given an atomic weight of 123.4. At a later date it was found that the correct atomic weight of cesium is 132.8.

(4) It stimulated further research work. Many problems were presented by the discovery of the periodic system which could only be solved in a satisfactory way by further study of the elements. In some cases such research is still being conducted, especially in the *rare earth elements*, which start with lanthanum of atomic weight 139 and finish with lutecium of atomic weight 175.

6. The Modern Periodic System

Most scientific laws have certain imperfections and limitations, and we find that the periodic law is no exception. It was pointed out in our description of the table that hydrogen has no place in the various groups of the elements. In addition, we observe certain exceptions to the arrangement of the elements in the order of their atomic weights. For example, tellurium is placed before iodine, in spite of the fact that the former has the higher atomic weight. There are other minor defects but the advantages of the periodic classification far outweigh these imperfections. It has been found that even some of the defects disappear when *atomic numbers* rather than atomic weights are made the basis of classification. When atomic numbers are made the basis of classification, the periodic law becomes: *The properties of elements are periodic functions of their atomic numbers.*

EXERCISES

1. Discuss the classification of the elements into metals and nonmetals. What is the chief defect of this system?
2. (a) What is meant by a triad?
   (b) What contribution did Döbereiner make to the classification of the elements?
3. Write a note on the contribution made by Newlands to the problem of classifying the elements.
4. Write a short essay on the Periodic System of Mendeléeff.

5. (a) What is the Periodic Law?
   (b) Show how the valence of elements is a periodic function of their atomic weights.
6. Write a note on the relations inside the groups.
7. Discuss the advantages of the periodic system.
8. What is the modern basis of classifying the elements, and what improvement is it as compared to the use of atomic weights as the basis of classification?

CHAPTER LIII

THE HALOGENS

All chemical elements may be arranged in families, the members of which are closely related. Fluorine, chlorine, bromine and iodine make up a remarkable family of non-metallic elements. They are found in Group VII of the Periodic Table, and the group as a whole is often called the *halogens*, which means *salt producers*. These elements have a very strong tendency to combine with metals and with hydrogen to form compounds known respectively as fluorides, chlorides, bromides and iodides, which are often called the *halides*. Some of the halides, such as sodium chloride (common salt), potassium chloride and silver bromide, are of great commercial importance. Chlorine has already been considered in Chapter 29, and we shall now study fluorine, bromine and iodine.

FLUORINE (F_2)

1. Occurrence

Fluorine does not occur in the free state but it does occur abundantly in the minerals *fluorspar*, CaF_2, and *cryolite*, Na_3AlF_6. Traces of fluorine compounds are found in the bones and enamel of teeth, and small quantities have been detected in the blood, milk, and brains of animals. Minute amounts of fluorine compounds are also found in sea water.

2. Preparation

Fluorine, the most active element known, was not prepared until 1886. This difficult task was accomplished by a brilliant French chemist, Moissan, who also produced diamonds from pure charcoal. He obtained fluorine by the electrolysis of potassium hydrogen fluoride, KHF_2, dissolved in hydrogen fluoride, H_2F_2, in an apparatus constructed of an alloy of platinum (Pt) and iridium (Ir). Fluorine was given off at the positive electrode.

3. Physical Properties

Fluorine is a pale greenish-yellow gas, which may be condensed to a liquid at —187° C. It has an irritating odour and is slightly heavier than air. Fluorine does not dissolve in water, but it reacts vigorously with water.

4. Chemical Properties

Fluorine is a very active element, reacting with all the elements except oxygen, chlorine, nitrogen and the inert gases. As a rule, the action between fluorine and another element is marked by the rapid giving off of heat and light. Fluorine decomposes water with the liberation of a mixture of oxygen and ozone:

$$2\ H_2O + \underset{\text{(fluorine)}}{2\ F_2} \longrightarrow \underset{\substack{\text{(hydrogen}\\\text{fluoride)}}}{4\ HF} + O_2$$

$$3\ H_2O + 3\ F_2 \longrightarrow 6\ HF + \underset{\text{(ozone)}}{O_3}$$

Fluorine combines explosively with hydrogen, even in the dark. It is interesting to know that fluorine replaces all other halogens and all other non-metals from their compounds with hydrogen or the metals. For example, fluorine displaces chlorine from sodium chloride, as shown by the following equation.

$$F_2 + 2\ NaCl \longrightarrow 2\ NaF + Cl_2$$

5. Uses

There are no uses for fluorine itself, but some of its compounds are very useful. *Ammonium fluoride*, NH_4F, is used as a disinfectant, and *sodium fluoride*, NaF, is an insecticide. *Cryolite*, Na_3AlF_6, is necessary in the production of metallic aluminum from bauxite. *Dichloro-difluoro-methane*, CCl_2F_2, known by the trade name of *freon*, is an important refrigerant.

6. Hydrofluoric Acid, H_2F_2

One of the most useful compounds of fluorine is hydrofluoric acid. Because this acid attacks glass, it must be kept in bottles made of gutta-percha or of ceresin, a sort of hard mineral substance. Hydrogen fluoride is prepared in the laboratory by the action of concentrated sulphuric acid on a fluoride such as calcium fluoride, CaF_2. The equation for this reaction is:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2F_2\uparrow$$

Hydrofluoric acid is formed when the gas hydrogen fluoride is passed into water.

Hydrofluoric acid is very poisonous and produces serious burns when it comes in contact with the skin. This acid is very weakly ionized in water.

$$H_2F_2 \rightleftharpoons 2\ H^+ + 2\ F^-\ .$$

Hydrofluoric reacts with silicon compounds, and so it attacks glass, which is a complex mixture of silicates of calcium and sodium. Since hydrofluoric acid attacks glass, it is useful for etching. The action of hydrofluoric on glass can be explained by the following equations:

$$\underset{\text{(calcium silicate)}}{CaSiO_3} + 3\ H_2F_2 \longrightarrow \underset{\text{(soluble)}}{CaF_2} + SiF_4\uparrow + 3\ H_2O$$

$$\underset{\text{(sodium silicate)}}{Na_2SiO_3} + 3\ H_2F_2 \longrightarrow \underset{\text{(soluble)}}{2\ NaF} + SiF_4\uparrow + 3\ H_2O$$

For etching, the glass is covered with a film of wax, and the design to be etched on the glass is drawn on the waxed surface with a stylus. The acid is then applied to the surface and in a short time the glass is etched. The wax is then removed with turpentine. Hydrofluoric acid is used to etch graduations on thermometers, burettes, etc. It is also used to make the frosting on the inside of electric light bulbs. The analytical chemist uses hydrofluoric acid to dissolve silicates or materials containing silicates, when he does certain determinations.

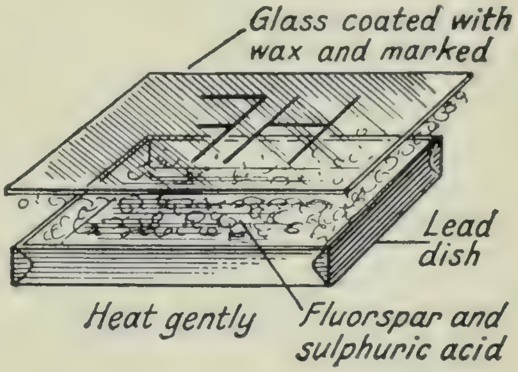

Glass coated with wax and marked
Lead dish
Heat gently
Fluorspar and sulphuric acid

Fig. 226—Etching Glass

BROMINE (Br_2)

1. Occurrence

Bromine was discovered about a century ago by the French chemist Ballard. The element occurs in nature as bromides, chiefly as magnesium bromide, $MgBr_2$, and sodium bromide, NaBr, which are found in many springs and salt deposits. The Stassfurt deposits in Germany and the salt waters of Michigan and Ohio are richest in bromides. Sea water also contains small amounts of bromides.

2. Preparation

Bromine is prepared commercially by the electrolysis of a solution of a bromide or by treating solutions of bromides with the more active element chlorine.

$$MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2$$

In recent years the demand for bromine has greatly increased due to its use in the preparation of ethylene bromide, $C_2H_4Br_2$.

This compound is a component of ethyl gasoline. A few years ago a plant was built on the Atlantic coast for the extraction of bromine from the ocean. It takes about 1800 gallons of sea water to produce one pound of bromine.

Bromine is usually prepared in the laboratory by heating a mixture of potassium or sodium bromide, manganese dioxide and dilute sulphuric acid in a retort. The equation for the reaction using potassium bromide, is as follows:

$$2\ KBr + 2\ H_2SO_4 + MnO_2 \longrightarrow K_2SO_4 + 2\ H_2O + Br_2\uparrow + MnSO$$

3. Physical Properties

Bromine is a dark-red, fuming *liquid* with a very disagreeable odour. In fact, the word bromine is derived from the Greek word meaning *stench.* Bromine vapour attacks the eyes very painfully and produces great irritation when inhaled. It is about three times as heavy as water and is moderately soluble in water, the resulting solution being known as bromine water.

4. Chemical Properties

Bromine reacts with hydrogen to produce hydrogen bromide.

$$H_2 + Br_2 \longrightarrow 2\ HBr$$

However, it does not react with hydrogen as violently as chlorine, which combines with hydrogen with explosive violence in sunlight. Bromine combines vigorously with certain elements to form bromides. For example, powdered antimony burns spontaneously in bromine, producing antimony bromide.

$$2\ Sb + 3\ Br_2 \longrightarrow 2\ SbBr_3$$

Phosphorus also reacts readily with bromine.

$$P_4 + 6\ Br_2 \longrightarrow 4\ PBr_3$$

5. Uses

Bromine is used in the preparation of certain important *dyes.* Considerable quantities of bromine are used in the manufacture of *tear-gases* or *lachrymators.* The use of bromine in the manufacture of ethyl gasoline has already been mentioned. Bromine is sometimes used by analytical chemists in reactions where an oxidizing agent is required in certain determinations.

6. Hydrobromic Acid, HBr

Hydrobromic acid is made by passing hydrogen bromide into water. Hydrogen bromide can be made by heating concentrated sulphuric acid with a bromide.

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr\uparrow$$

However, in addition to getting HBr, we also obtain some Br_2 and SO_2 because HBr is less stable than HCl and HF. In addition, concentrated sulphuric acid is an oxidizing agent, and so the following reaction takes place:

$$H_2SO_4 + 2\ HBr \longrightarrow 2\ H_2O + SO_2\uparrow + Br_2\uparrow$$

Pure hydrogen bromide can be obtained by dropping bromine upon a mixture of red phosphorus and water. The phosphorus and bromine react to form phosphorus tribromide, which reacts at once with the water, producing hydrogen bromide.

$$P_4 + 6\ Br_2 \longrightarrow 4\ PBr_3$$

$$\underset{\substack{\text{(phosphorus}\\\text{tribromide)}}}{PBr_3} + 3\ H_2O \longrightarrow 3\ HBr\uparrow + \underset{\substack{\text{(phosphorus}\\\text{acid)}}}{H_3PO_3}$$

Hydrogen bromide is a colourless gas. It is heavier than air and very stable in water. This gas, like the other hydrogen halides, fumes in moist air. It has an irritating odour, and does not burn in air. The gas does not support combustion, and when dry, it possesses no acid properties.

When hydrogen bromide is bubbled into water, hydrobromic acid is produced. This acid is quite active because it is highly ionized.

$$HBr \rightleftharpoons H^+ + Br^-$$

It is similar in chemical properties to hydrochloric acid, although being somewhat less stable. Hydrobromic acid reacts with metals, oxides of metals, and hydroxides, producing a group of salts, known as bromides.

The bromides of potassium and sodium are used in medicine as *sedatives*. Silver bromide, AgBr, is used extensively in *photography;* it is the material on the film which is sensitive to light.

IODINE (I_2)

1. Occurrence

Iodine was discovered in 1812 by the French chemist, Courtois, who obtained it from the mother-liquor of salts produced from burnt sea-weed, or kelp. When the liquid was heated with sulphuric acid in a retort, a violet vapour was produced which condensed in the form of brilliant crystals. Shortly after this discovery the name iodine was proposed for this substance because it is derived from the Greek word for violet.

Iodine occurs in sea-water, in sea-plants and sea-animals, and in the thyroid gland of man and animals. Most of the iodine of commerce is obtained from a compound called sodium iodate, $NaIO_3$, which is found in small amounts in Chile saltpetre (crude $NaNO_3$).

2. Preparation

When iodines are treated with bromine or chlorine, free iodine is liberated.

$$2\,NaI + Br_2 \longrightarrow 2\,NaBr + I_2$$
$$2\,KI + Cl_2 \longrightarrow 2\,KCl + I_2$$

Iodine is usually prepared in the laboratory by heating a mixture of potassium iodide and manganese dioxide with concentrated sulphuric acid.

$$2\,KI + 2\,H_2SO_4 + MnO_2 \longrightarrow K_2SO_4 + MnSO_4 + 2\,H_2O + I_2\uparrow$$

The iodine escapes from the reaction mixture as a purple vapour, which is condensed on a cold surface directly to the solid state.

3. Physical Properties

Iodine is a shining blackish-gray *solid*, which is nearly five times as heavy as water. It has a strong, rather unpleasant odour, and changes to the vapour state (sublimes) even at ordinary temperatures. This element is quite soluble in alcohol and in a water solution of potassium iodide (KI). We are all familiar with iodine in the form of *tincture* of iodine, which consists of iodine crystals dissolved in alcohol. A very small quantity of iodine colours starch solution a deep blue and this is a very delicate test for the element.

4. Chemical Properties

Iodine is the least active of all the halogens. However, it does react with a number of elements. For example, iodine combines vigorously with zinc, in the presence of moisture, to form zinc iodide.

$$Zn + I_2 \longrightarrow ZnI_2$$

Phosphorus burns in iodine vapour, producing phosphorus iodide.

$$P_4 + 6\,I_2 \longrightarrow 4\,PI_3$$

Iodine will react with hydrogen in the presence of finely divided platinum, which acts as a catalyst.

$$H_2 + I_2 \longrightarrow 2\,HI$$

5. Uses

Iodine is used in the manufacture of certain dyes and drugs which are very helpful to man. The largest consumer of iodine is the photographic industry which uses the two compounds, silver iodide and potassium iodide, in large quantities. Iodoform, CHI_3, is used in hospitals as an antiseptic.

Iodine is an essential constituent of the body. A small gland known as the thyroid gland contained in the bunch of cartilage at the front of the throat usually called the Adam's Apple, produces a compound known as thyroxin, which contains about 9.3 per cent of iodine. If iodine is not present in the diet, the thyroid gland cannot produce this compound, and so goitre results. Iodized salt is now prepared for table use, the small amount of sodium iodide (NaI) present in the salt being considered sufficient to guard against a natural deficiency in the regular food. Iodine is supplied by certain foods, such as spinach, lettuce, string beans, butter, milk, fish and other sea foods.

6. Hydriodic Acid, HI

Hydriodic acid is formed when hydrogen iodide comes in contact with water. Hydrogen iodide cannot be prepared by the action of sulphuric acid on iodides because it is even more unstable than hydrogen bromide. It is also oxidized readily by sulphuric acid. Hydrogen iodide can be prepared, however, by the reaction of red phosphorus, iodine, and water.

$$P_4 + 6\,I_2 \longrightarrow 4\,PI_3$$

$$PI_3 + 3\,HOH \longrightarrow 3\,HI + H_3PO_3$$

In addition, a water solution of HI may be produced by the reaction of iodine with a solution of hydrogen sulphide.

$$H_2S + I_2 \longrightarrow 2\,HI + S\downarrow$$

Hydrogen iodide is a colourless gas, which is very irritating to the throat. Like hydrogen bromide, it fumes in moist air. The gas is very soluble in water and is highly ionized, forming hydriodic acid. Hydrogen iodide is much heavier than air. It is less stable than hydrogen chloride or hydrogen bromide, and decomposes, upon being heated, into hydrogen and iodine.

$$2\,HI + \text{heat} \longrightarrow H_2 + I_2$$

A solution of hydriodic acid turns brown in sunlight when exposed to air. This is caused by the oxidation of HI by the oxygen of the air, forming free iodine and water.

$$4\ HI + O_2 \longrightarrow 2\ H_2O + 2\ I_2$$

EXERCISES

1. (a) What is the meaning of the term halogen?
   (b) Make a list of the elements in the halogen family.
2. Write a note on the occurrence of fluorine.
3. (a) Why is it so difficult to prepare fluorine?
   (b) Who was the first chemist to prepare this gas?
   (c) Discuss briefly how he obtained the element.
4. (a) Tabulate *five* physical properties of fluorine.
   (b) Tabulate *three* chemical properties of fluorine. Write equations to illustrate your answer whenever possible.
5. Write a note on the uses of fluorine.
6. Discuss the usefulness of hydrofluoric acid.
7. (a) Discuss bromine under the headings: (1) occurrence; (2) preparation; (3) physical properties; (4) chemical properties; (5) uses.
   (b) Write an equation for the preparation of hydrogen bromide.
8. Discuss iodine under the headings: (1) occurrence; (2) preparation; (3) physical properties; (4) chemical properties; (5) uses.
9. Write a note on hydrogen iodide.

CHAPTER LIV

PHOSPHORUS

The element phosphorus is one of a family of chemical elements found in Group V of the Mendeléeff Periodic Table. The other members of this family are nitrogen, arsenic, antimony and bismuth.

1. Occurrence

Phosphorus is the element which shines in the dark, and its name is derived from the Greek, meaning the "light bringer." It was accidentally discovered by a German alchemist named Brand about 1669. Phosphorus occurs in nature in large quantities as phosphates in a mineral known as *apatite*, $Ca_3(PO_4)_2$. Calcium phosphate is also present in fertile soil. Bones and teeth contain about 30 per cent phosphorus as calcium phosphate. Nerves and muscles also contain this element. The source of the phosphorus which is present in our bodies is the soil. Plants take it up and man obtains it directly by eating plants or indirectly from the tissues of plant-eating animals. Scientists have estimated that the adult human body contains about 700 grams (more than a pound and a half) of phosphorus. Of this amount about 600 grams occurs in the skeleton. The remainder of the phosphorus is in the tissues and in the blood plasma, chiefly in the form of phosphates.

2. Preparation

Phosphorus is manufactured from phosphate rock (natural calcium phosphate). This material is pulverized and mixed with the correct amounts of carbon and sand (silicon dioxide). The mixture is fed continuously into an electric furnace, entering at the top through a worm feed as shown in Fig. 227. The discharge of an alternating current between the carbon electrodes furnishes the extremely high temperature which is needed to bring about the conversion of the phosphate into free phosphorus. Calcium silicate, produced in the reaction, melts to form a slag, which is drawn off at the bottom of the furnace. The carbon monoxide and phosphorus vapour escape through an opening near the top of the furnace. The phosphorus vapour is condensed to the solid state by means of cold water. The equation for the reaction is:

$$2\ Ca_3(PO_4)_2 + 6\ SiO_2 + 10\ C \longrightarrow 6\ CaSiO_3 + 10\ CO\uparrow + P_4\uparrow$$

The above equation is rather complicated, and so we shall try to explain it by considering separately what happens to the starting materials. The calcium phosphate decomposes, due to the heat of the furnace, into calcium oxide (CaO) and phosphorus pentoxide (P_2O_5).

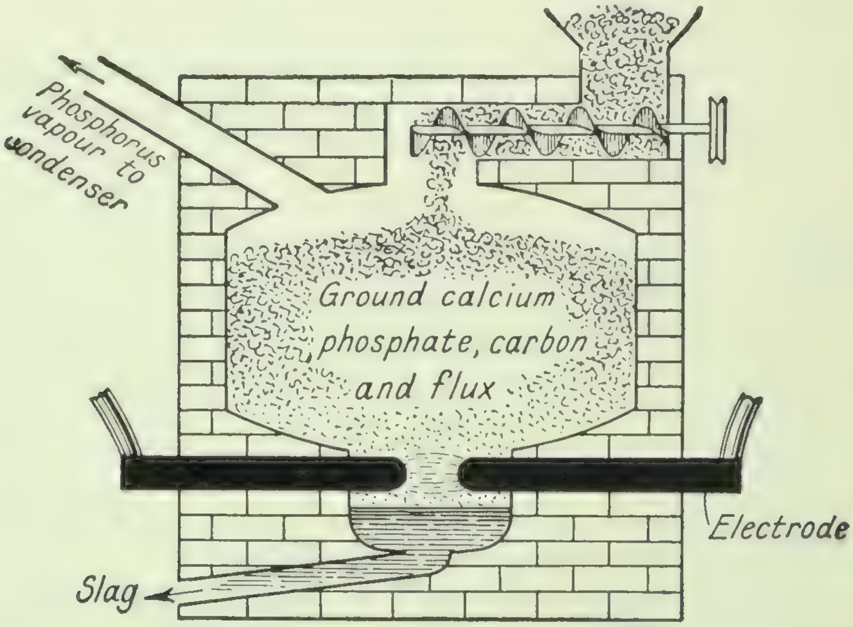

Phosphorus vapour to condenser
Ground calcium phosphate, carbon and flux
Electrode
Slag

FIG. 227—MANUFACTURE OF PHOSPHORUS

$$Ca_3(PO_4)_2 \longrightarrow 3\ CaO + P_2O_5$$

The calcium oxide combines with the silicon dioxide to produce calcium silicate ($CaSiO_3$), which is the slag.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

The phosphorus pentoxide (P_2O_5) is reduced by the carbon to free phosphorus.

$$2\ P_2O_5 + 10\ C \longrightarrow 10\ CO\uparrow + P_4\uparrow$$

The phosphorus is purified and made into sticks, which are kept under water to prevent spontaneous combustion.

3. Properties

Phosphorus is an *allotropic* element; it occurs in two forms, the *white* (sometimes known as yellow) and the *red*. These two varieties of phosphorus differ greatly in their properties. The outstanding differences between the two forms of phosphorus are shown in Table 30.

TABLE 30—PROPERTIES OF WHITE AND RED PHOSPHORUS

White	Red
1. Slight yellow colour.	1. Chocolate red powder.
2. Melts at 44° C.	2. Sublimes when heated, melts at 600° C. (under pressure).
3. Glows in dark when exposed to air, known as *phosphorescence*.	3. Does not glow.
4. Oxidizes rapidly in air, has a low kindling temperature and must be kept under water. $P_4 + 5O_2 \longrightarrow 2\ P_2O_5$	4. Only burns when heated to a high temperature (250° C.).
5. Very poisonous.	5. Not poisonous.
6. Soluble in CS_2.	6. Insoluble in CS_2.

4. Uses

(1) MATCHES. White phosphorus was used in making matches for many years until it was discovered that phosphorus vapours produce a disease which brings about a disintegration of the bones; the bones of the jaw are especially affected. Red phosphorus is now used on the boxes of safety matches; phosphorus sesquisulphide, P_4S_3, is used as one of the ingredients of the tips of matches of the "strike anywhere" variety.

(2) RAT POISON. Phosphorus is sometimes used in rat poison.

(3) SMOKE SCREENS. The most common smoke screen used in warfare is produced by burning phosphorus. The white smoke produced consists of finely divided particles of phosphorus oxides, chiefly the pentoxide.

(4) INCENDIARY BOMBS. Some types of incendiary bombs used during World War II contained phosphorus.

5. Phosphoric Acid, H_3PO_4.

The burning of phosphorus in oxygen or an excess of air produces a white smoke which consists of very fine particles of a solid, phosphorus pentoxide, P_2O_5.

$$P_4 + 5\ O_2 \longrightarrow 2\ P_2O_5$$

When this oxide is added to water, it forms phosphoric acid, H_3PO_4, often called *orthophosphoric acid.*

$$P_2O_5 + 3\ H_2O \longrightarrow 2\ H_3PO_4$$

Phosphoric acid has three replaceable hydrogen atoms in the molecule and is, therefore, a tribasic acid. It forms three types of salts, examples of which are given below:

Na_3PO_4	normal sodium phosphate (trisodium phosphate).
Na_2HPO_4	disodium phosphate.
NaH_2PO_4	monosodium phosphate.

6. Fertilizers

Plants take carbon dioxide and a small quantity of oxygen from the air, but otherwise they depend largely on the soil for nourishment. Mineral matter and organic matter are the chief plant foods contained in the soil. Since these substances are continually removed from the soil by growing plants and by

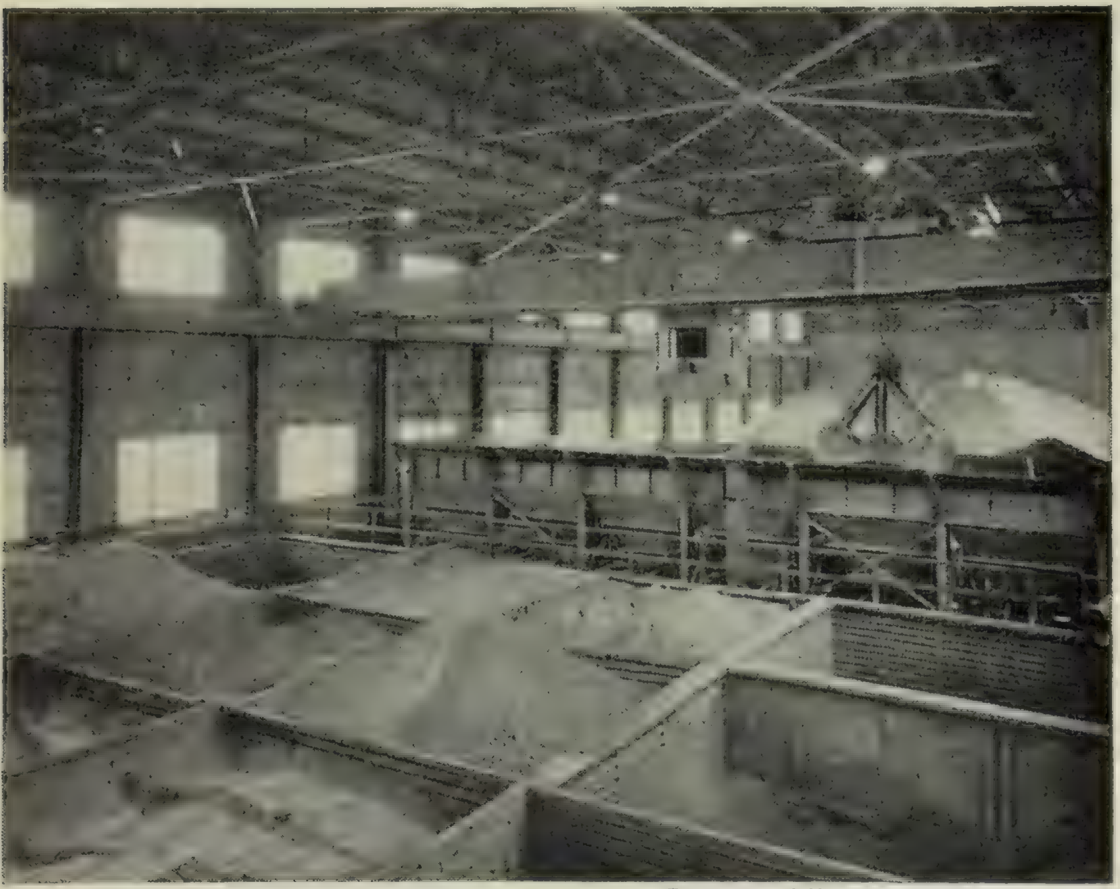
Courtesy of Canadian Industries, Ltd.

FIG. 228—A SOIL CHEMIST AT WORK ANALYZING SOIL FROM VARIOUS PARTS OF CANADA

drainage, it is necessary that they be replaced from time to time. This process is known in agriculture as fertilizing the soil.

The three essential elements required by plants are nitrogen, potassium, and phosphorus. These elements are obtained by using mixed fertilizers, which usually contain calcium phosphates, nitrogenous matter, and compounds of potassium. Several other elements, often referred to as secondary elements, must be added to the soil: these are sodium, calcium and magnesium. Each soil must be analyzed to determine what elements are lacking, and, of course, various crops have somewhat different requirements. For example, wheat and other cereal crops need a soil rich in phosphates, while potatoes require more potassium. Fig. 228 shows a chemist at work testing samples of soil from various parts of Canada. Fig. 229 shows how fertilizers are mixed in large mechanical mixers.

The phosphorus in most commercial fertilizers is present as *superphosphate*, which is obtained by treating phosphate rock



Courtesy of Canadian Industries, Ltd.

FIG. 229—TODAY'S SCIENTIFICALLY COMPOUNDED FERTILIZERS ARE MIXED IN LARGE MECHANICAL MIXERS AND CURED IN LARGE BINS AS SHOWN IN THE FOREGROUND. THE HUGE TONNAGES HANDLED IN SUCH A PLANT AS PICTURED REQUIRE A GREAT DEAL OF HEAVY MACHINERY. NOTE THE PILE OF BULK SUPERPHOSPHATE IN THE REAR; ALSO THE TRAVELLING ELECTRIC CRANE IN MIDDLE RIGHT OF PICTURE

(which consists chiefly of tri-calcium phosphate, $Ca_3(PO_4)_2$, with sulphuric acid.

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 \longrightarrow Ca(H_2PO_4)_2 + 2\ CaSO_4$$

The monocalcium phosphate, $Ca(H_2PO_4)_2$, is quite soluble in water, and so can be readily taken up in solution by plants through their roots. The calcium sulphate, $CaSO_4$, is not removed in commercial fertilizer manufacture as it does no harm, and, in some cases, may be beneficial to the soil.

Triple or treble superphosphate is produced by treating rock phosphate with phosphoric acid, H_3PO_4, rather than sulphuric acid. This produces almost three times the quantity of monocalcium phosphate from a given weight of rock phosphate as that obtained with sulphuric acid. Ground-up bone is another source of calcium phosphates, and, in addition, it contains nitrogen, giving it added value. However, the supply is not sufficient to meet the demand, and so rock phosphate remains the chief source of phosphates for commercial fertilizers. "Slags" which are formed in the production of steel are a further source of phosphates and are used to increase the amount of phosphorus in the soil.

The nitrogenous matter is obtained from various chemicals containing nitrogen and from decomposed animal matter. The following chemicals supply commercial fertilizers with nitrogen: sodium nitrate, $NaNO_3$, calcium nitrate, $Ca(NO_3)_2$, potassium nitrate, KNO_3, ammonium nitrate, NH_4NO_3, ammonium sulphate, $(NH_4)_2SO_4$, ammonium chloride, NH_4Cl, ammonium phosphates, $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$, urea, $(NH_2)_2CO$, and calcium cyanamide, $CaCN_2$. Nitrogen is also put into the soil by the production of legume plants (alfalfa, beans, and peas), which return nitrogen to the earth.

Potassium compounds are found in natural deposits in France and Germany, but are rare on this continent.

Fertilizers are manufactured in Canada on a much larger scale than is generally known. Ammonium sulphate, ammonium phosphate, superphosphate, cyanamide, and mixed fertilizers are all made in different parts of the Dominion in large quantities. As the industry is comparatively new in Canada, the latest equipment and processes of manufacture are in use, resulting in high quality products.

Science has known for some years that plants will grow without soil. Growing a garden without soil is known as *hydro-*

ponics, and for several years past many people have grown fresh fruits and vegetables by this method. The soil is replaced by some inert medium like sand, gravel or cinders, to support the roots, and the minerals required by the plants are furnished by the application of a dilute solution of chemicals. Fig. 230 shows a chemical garden on a roof top.

FIG. 230—A CHEMICAL GARDEN ON A ROOF TOP

EXERCISES

1. Write a note on the occurrence of phosphorus.
2. Describe briefly the preparation of phosphorus from phosphate rock. Illustrate your answer with a labelled diagram and write the equation for the reaction.
3. Compare and contrast the properties of white and red phosphorus.
4. Write a note on the uses of phosphorus.
5. (a) Write the formula for orthophosphoric acid.
   (b) What is the anhydride of this acid?
   (c) Write the formulas and names for the three sodium phosphates.
6. (a) What is a fertilizer?
   (b) Why is it necessary to add chemical fertilizers to the soil?
   (c) What are the essential elements required by plants?

7. (a) What is the composition of a mixed fertilizer?
   (b) Name the secondary elements required by plants.
   (c) What determines the type of fertilizer used by a farmer?
8. Write a note on superphosphate.
9. (a) Make a list of five substances which are used in commercial fertilizers to supply nitrogen.
   (b) What is the source of potassium for a mixed fertilizer?
10. Write a short note on hydroponics.

Chapter LV

COLLOIDS

1. The Nature of Colloids

Many of the materials used by us every day belong to the colloidal state of matter. These substances are known as *colloids*, and the study of materials in such a state is called *colloidal chemistry*. This new and interesting field of chemistry was opened up by the researches of an English chemist, Graham, in 1861. He had studied the diffusion of gases with considerable success, and he decided to investigate the diffusion of solids in liquids. Graham found that substances such as cane sugar, acids, bases, and salts, diffuse rapidly through a solvent such as water. These substances he called crystalloids. However, he discovered that certain materials, such as starch, aluminum hydroxide, tannin, albumen and gelatin, diffused very slowly through water. These substances he called *colloids*—derived from the Greek, meaning glue-like.

It was soon discovered by colloidal chemists that the size of the particle is a very important factor; it is used as a basis for defining the colloidal state. One millionth of a millimetre has been selected as the unit for measuring the diameter of colloidal particles; it is known as one *millimicron* (uu). It is generally considered that a material is in the colloidal realm if the diameter of its particles is greater than *five* millimicrons but less than a hundred millimicrons. Substances in true solution are considered to be in the molecular or ionic state, and the diameters of molecules range from about one-half a millimicron to about five millimicrons. The particles of ordinary suspensions vary in diameter from about one hundred millimicrons to ten thousand millimicrons. It is important to remember that to speak of a particular substance as a colloid is incorrect. Any substance may be obtained in colloidal form if we can subdivide it to the right degree.

In studying solutions it was found that the substance which dissolved was called the solute, and the substance which did the dissolving was known as the solvent. In colloidal chemistry the *disperse phase* corresponds to the solute, and the *dispersing* *medium* corresponds to the solvent. The disperse phase may be a gas, a liquid, or a solid, and the dispersing medium can also be any one of the three states of matter. However, it is impossible to have a gas dispersed in another gas as the particles are always in the molecular state, and so it is only possible to have eight types of colloidal dispersions. The most common type of colloidal dispersion is that of a solid in a liquid: starch in water is a good example of this type. A liquid dispersed in another liquid is also quite common and such a system is called an emulsion. Milk is an emulsion of butter-fat, dispersed in water.

2. Properties of Colloids

Some materials disperse at once if placed in a liquid of the proper type. This process is called *peptization.* Glue, starch, gelatin and albumen are examples of substances which naturally form colloidal suspensions when mixed with water or some other liquid. Such substances are known as *lyophilic* colloids (hydrophilic, if water is the liquid used). Lyophilic colloids tend to *adsorb* much of the liquid to become highly solvated. As a rule, most lyophilic colloids are organic substances. On the other hand, elements or inorganic compounds usually require special methods to change them into stable colloidal suspensions. Such substances are known as *lyophobic* colloids (hydrophobic, if water is the liquid used). Lyophobic colloids are not solvated.

When a beam of light goes through a true solution, no path of light is observed. However, if the light is passed through a colloidal suspension such as colloidal ferric hydroxide, the path of the beam is quite evident. The particles scatter the light making its path visible. This phenomena is known as the *Tyndall effect.* The result with a colloidal system is very much like that observed when a beam of light passes through the air of a darkened room; one becomes aware of the dust particles suspended in the air. Two colloidal chemists, Siedentoff and Zsigmondy, used the Tyndall effect along with a microscope to produce the *ultramicroscope,* which has been of great value in the study of colloids.

Colloidal particles can be observed by means of the ultramicroscope. When examined in this way, the particles appear to move about continuously, and the path traced out by a colloidal particle is a zigzag one. This movement, discovered by an English botanist, Robert Brown, in 1827, and known as the

Brownian movement, is due to the bombardment of the colloidal particles by the molecules of the dispersing medium (water). The Brownian effect is important evidence in support of the kinetic molecular theory.

An important property of colloidal particles is that they usually carry an electric charge. The charge on the particle can be determined by placing the suspension in a cataphoresis apparatus (contains a positive and negative electrode). In such an apparatus the colloidal particles move slowly towards the electrode of opposite charge, and this process is known as *cataphoresis.* In a given colloidal dispersion all the particles have the same charge. As a rule, the particles of colloidal suspensions of metallic oxides, hydroxides, and many dyes carry a *positive charge.* On the other hand, metallic sulphides and most metals carry a *negative charge.*

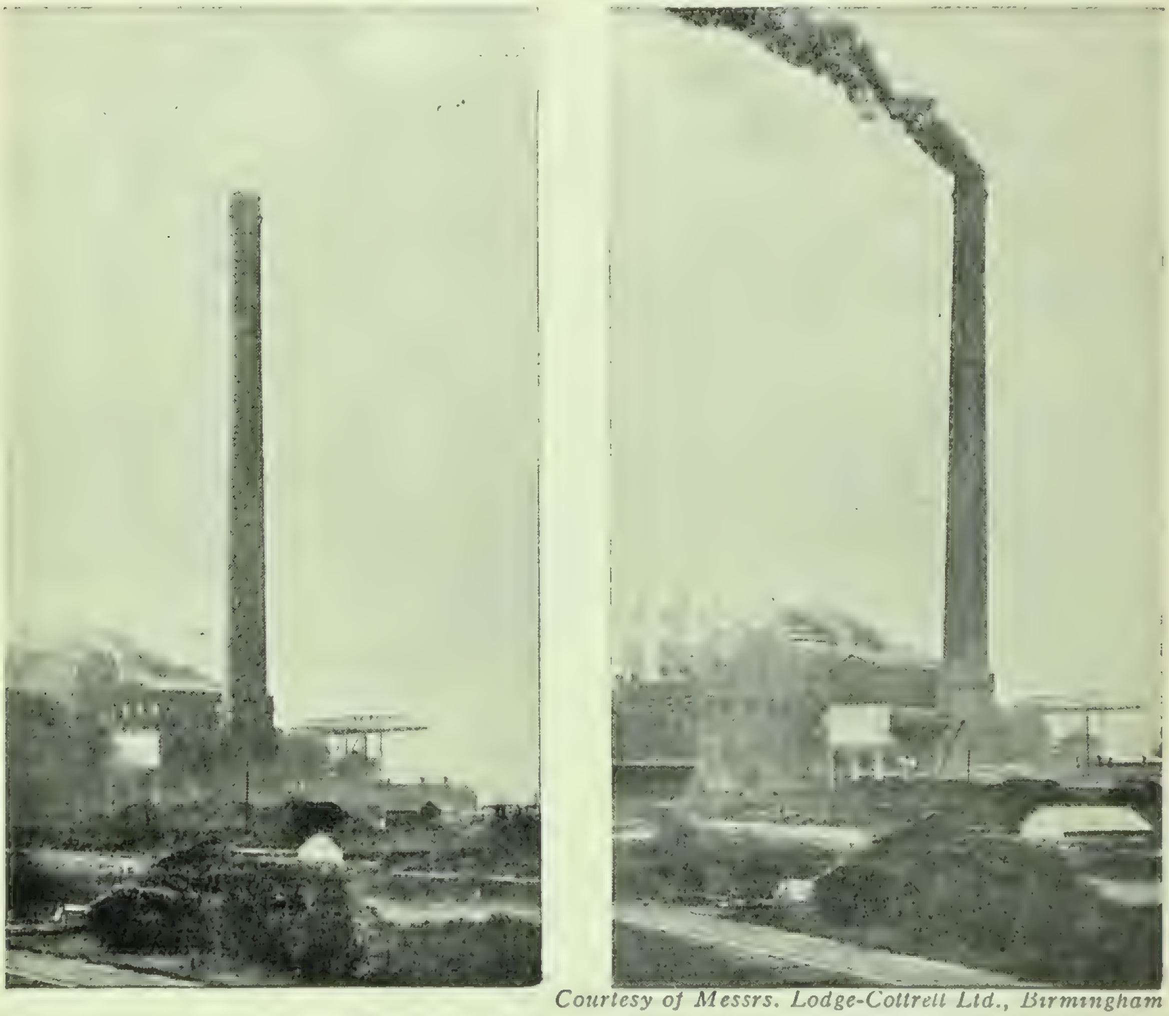
Another property of colloidal systems is that the particles do not settle out on standing. This permanence of colloidal suspensions is due to the electrical charge carried by the particles. Like charges repel each other, and as long as the particles have their charge, there is no clustering of the particles to form a precipitate. Bombardment of the particles by the dispersing medium (water) is another reason why colloidal particles do not settle out on standing.

3. Precipitation of Colloids

If the charge on the colloidal particles is neutralized, the particles tend to cling together to form clusters, which are heavy enough to settle to the bottom of the container. This process is known as precipitation or *coagulation.* The souring of milk is a good example of coagulation. Milk contains the protein casein in colloidal form. When milk stands for some time, the lactose (a sugar) in the milk is changed to lactic acid, the ions of which neutralize the charge on the casein particles, and the casein coagulates out as a curd. The addition of electrolytes, then, is one method of precipitating colloids. It has been found that trivalent ions, such as aluminum ions (Al^{+++}), coagulate negative colloids better than divalent ions, such as barium ions (Ba^{++}). Barium ions, in turn, coagulate negative colloids better than monovalent ions, such as sodium ions (Na^{+}).

Another way of precipitating colloids is to add another colloid of the opposite charge. For example, colloidal ferric hydroxide particles carry positive charges, and they can be precipitated by adding some colloidal silicic acid, the particles of which carry negative charges.

Another method of precipitating colloids was devised by an American chemist, *Cottrell*, and is named after him. It is especially good for removing particles suspended in fumes, fogs and smokes. The gases containing very fine dust particles, are passed up a tube, about eight inches in diameter, in which a copper wire or a metallic chain is hung. A high-tension direct current (75,000 to 100,000 volts) is passed from the wire to the surrounding tube. As the gases pass through the apparatus, known as a *Cottrell precipitator*, the fine solid particles, which are present in the gases, become electrically charged due to the silent discharge of the central wire or chain. The tube has the opposite electrical charge to the wire, and the solid particles (now having the same charge as the wire) are attracted to the tube. The particles deposit on the walls of the tube and are



Courtesy of Messrs. Lodge-Cottrell Ltd., Birmingham

FIG. 231—SMOKE ABATEMENT: A POWER STATION

Left: with Cottrell precipitator in action. Right: without Cottrell precipitator in action.

made to fall off into a box at the bottom of the tube on rapping. The Cottrell process is used to eliminate the smoke nuisance, which is produced by factory chimneys as shown in Fig. 231. It is also used to remove fine particles of copper from the smoke coming out of the chimneys in copper smelters. The process is also applied to sulphuric acid mists, cement furnaces, air conditioning, and other uses.

Small amounts of certain colloids (lyophilic), when added to certain other colloids (lyophobic), tend to protect the latter from coagulation. Colloids which protect other colloids from coagulation are known as *protective colloids.* Gelatin, albumen, agar, dextrin, and gum-arabic are examples of this type of colloid.

$$\mathbf{NaCl + AgNO_3 \longrightarrow AgCl\downarrow + NaNO_3}$$

As shown by the above equation, silver chloride (AgCl) usually coagulates and settles out of suspension very rapidly. However, if a very small amount of gelatin is added to the silver nitrate solution before being added to the sodium chloride solution, the particles of silver chloride (colloidal) remain in suspension for a long time.

It is believed that the protective colloid forms a thin film around the lyophobic colloid, and so the particles are prevented from coming together to form larger particles. Protective colloids find many applications in industry. For example, the colloidal particles of silver bromide, AgBr, the light sensitive substance in photographic films, is made smooth and fine by the protecting action of gelatin. Gelatin also acts as a protective colloid in the manufacture of ice cream. It prevents the formation of large, gritty ice crystals, and produces a "smooth and velvety" product.

There are several terms used by colloidal chemists which should be considered here. A colloidal system before coagulation is known as a *sol,* whereas after coagulation the system is known as a *gel.* Sometimes the coagulated materials set to form a semi-solid, known as a *jelly.*

4. Dialysis

Dialysis is a method worked out by Graham for the separation of crystalloids from colloids. He discovered that crystalloids diffuse through a liquid much faster than do colloids, and this is the property upon which dialysis is based. For example, a colloidal starch suspension can be separated from a sodium chloride (crystalloid) solution by dialysis. The mixture is placed in a sack, made of parchment paper or cellophane, and suspended in a beaker of distilled water. The salt solution goes through the walls of the sack, while the starch does not. By putting fresh distilled water in the beaker every day, the salt solution is soon removed from the starch, and a pure starch suspension is left in the sack. This method of purifying colloids is extensively used, especially by bio-chemists in their studies of plant and animal materials of a colloidal nature.

5. Adsorption

Adsorption is the process by which substances are held on the surfaces of solids and liquids. Several examples of this process are encountered in the study of elementary chemistry. For example, soap *adsorbs* dirt in the washing of clothes or the skin. Charcoal adsorbs poisonous gases, such as chlorine. Again, bone-black or animal charcoal adsorbs coloured materials in the sugar refining process. Adsorption is a surface phenomenon, and so materials in the colloidal state are much used for this purpose as they have extremely large surface areas.

6. Applications of Colloids

There are many applications of colloidal chemistry in industry and in everyday life. For example, the following materials are colloidal in nature: rubber, glue, leather, milk, clay, paint, jelly, ink, soap, adhesives, and cheese. Blood and lymph are essentially colloidal in nature. Such important industrial processes as the manufacture of *explosives*, of *photographic films*, of *bricks* and *other ceramic products*, the production of *cement*, and many other processes involve colloidal reactions.

EXERCISES

1. Discuss the nature of colloids under: (a) the work of Graham,
   (b) the size of the particle,
   (c) types of colloidal systems.
2. Write short notes on the following: peptization, lyophilic colloids, Tyndall effect, Brownian movement.
3. (a) What is cataphoresis?
   (b) Give one example of a negative colloid and one of a positive colloid.
   (c) Why are most colloidal suspensions so permanent?
4. Discuss the methods of precipitating colloids.

5. Discuss protective colloids under: (a) what they are,
   (b) explanation of their action,
   (c) applications of.
6. Define the terms: sol, gel, jelly.
7. Describe an experiment which illustrates the process of dialysis.
8. Write a note on adsorption.
9. Write a note on the applications of colloids in industry and everyday life.

CHAPTER LVI

SILICON AND BORON

SILICON (Si)

1. Occurrence and Importance

Column IV of the periodic table of the elements has two elements, carbon, atomic weight 12, and silicon, atomic weight 28; these are very important to man and, indeed, to all life. The importance of carbon to life processes and the many compounds of carbon are discussed in previous chapters of this book. Silicon, on the other hand, contributes directly to the building of the bodies of only a few organisms, but silicon compounds form much of the platform of solid earth or soil on which plants grow or animals walk. Analytical chemists and others have been able to determine the average composition of the crust of the earth to a depth of ten miles. It is known that oxygen is the most abundant of all elements: then comes silicon, followed by aluminum. Carbon is in thirteenth place. The study of the carbon compounds has given rise to organic chemistry, and the study of silicon compounds is part of the subject of mineralogy. A *mineral* is a naturally occurring chemical compound in whose formation the life processes of a living thing has played no part. Silicon enters into the make-up of the bulk of all minerals. *Rocks*, which are simply aggregates of different minerals, contain commonly about 60% silicon. Some of the minerals, particularly some useful to man, are discussed in a later section of this chapter.

Silicon and carbon both have valences of four; for example, two compounds are $SiCl_4$, silicon tetrachloride, and CCl_4, carbon tetrachloride. Each combines readily with oxygen and other elements, but some important differences are found. One of the most outstanding is the tremendous number of carbon compounds. Silicon enters into many compounds but the known compounds are only a small fraction of those containing carbon. Something of the way in which silicon occurs in nature was indicated in the first paragraph of this chapter. It is quite obvious that the large proportion of oxygen in the earth's crust is not in the gaseous state but is combined with other elements.

Silicon is not found in the free state in nature. With a minor exception all the silicon is combined with oxygen. If it is not combined with oxygen alone, silicon is combined with oxygen and one or more of the other elements.

The oxide of silicon has the chemical name of *silica* and the mineral name *quartz.* It is *silicon dioxide,* SiO_2. Pure quartz is a clear glassy substance which is harder than glass. It is sometimes found in nature as six-sided crystals. Some quartz is cut in a fashion similar to that in which a diamond is cut. Such material is much inferior to diamond in hardness and is known as rhinestone, Brazilian diamond, Alaska diamond, or as "crystal." Quartz crystals may be coloured by impurities. Amethyst is purple and is cut for jewelry. Yellow or brownish quartz is known as citrine, or Spanish topaz when cut. Much quartz, particularly that found in gold-bearing veins, is milky white or bluish.

The six-sided crystals are not common, but quartz without crystal faces is common in many rocks, for example, in a *granite.* As the granite is worn away by the action of running water, the quartz is released and rounded to form *sand* grains. Under suitable conditions of formation a sand may be almost 100 per cent SiO_2. Such sand may be used in the manufacture of glass.

Silica melts at about 1700° C. to a clear liquid. This liquid may be chilled to a colourless glass, which is occasionally used for making laboratory apparatus. This glass, because of its high temperature of fusion, is expensive to make, but it has an unusual resistance to change of temperature. If heated to a red heat and plunged into water, it does not shatter as does ordinary glass. Because of its resistance to high temperatures, silica is used to line metallurgical furnaces.

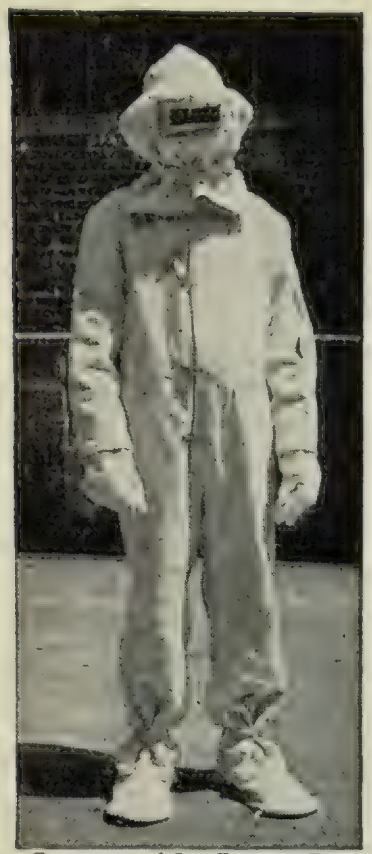
Although quartz is a common mineral, more complex compounds of silicon are more abundant. In these compounds silicon plays with oxygen the role of an acid-forming radical, and such compounds are known as *silicates.* Several kinds of silicates may be recognized and these are given diverse names, but certain phenomena give complications which cause most silicates to be given formulae, so unlike those ordinarily found in inorganic compounds that a full discussion of them is out of place here. However, several may be mentioned. The commonest of all minerals is *feldspar*, which forms about 60 per cent of the earth's crust. The one name really covers several minerals which are silicates of sodium, potassium, calcium and aluminum.

The potassium feldspar has a formula $KAlSi_3O_8$, which is really a simple formula among silicate minerals. This particular feldsspar when pure is used as a *glaze* for *pottery* and some varieties, known as "dental spar," are used for the porcelain of artificial teeth.

Some silicates have combined water and others contain a hydroxyl (OH) group. The silicates with combined water are mostly soft minerals. *Talc*, which is *hydrous* magnesium silicate, $H_2Mg_3(SiO_3)_4$, is ground to make talcum powder, as filling for cloth or paper. Impure varieties are sawed to make the *soapstone* desk tops seen in some chemical laboratories.

Courtesy of The Worcester Royal Porcelain Co. Ltd.

FIG. 232—DECORATING POTTERY



Courtesy of La France Fire Engine and Foamite, Ltd.

FIG. 233—ASBESTOS IS AN EXCELLENT HEAT INSULATOR

This asbestos suit is used by firemen to fight crash fires at airports, and other very hot fires such as those in oil fields.

The *clay* minerals are *hydrous* aluminum silicates. Contrary to what might be expected, clay minerals are not used as a source of aluminum. Most clays form a paste when mixed with water, and so they may be moulded into shapes such as bricks, sewer tile, or pottery objects. When fired in a suitable kiln, objects moulded from clay become rock-hard and the water expelled by the heating does not again soften the object. Some clays are able to adsorb impurities from solutions; others have the remarkable property of adsorbing fats and oils. *Fuller's earth* is used to de-fat cloth. Just why some clays have this remarkable property is not known.

Some silicate minerals have properties which make them useful for special purposes. *Asbestos* is a use name for several minerals capable of being separated into thin and flexible fibres. The asbestos mined in Quebec is *chrysotile*, a variety of serpentine, with the formula $H_4Mg_3Si_2O_9$. The fibres of asbestos may be spun like flax, and because the mineral resists heat and is a poor conductor of electricity, it has extensive use not only as a fire resistant material but also in electrical appliances. *Mica* is the name given to a group of minerals found in many rocks. Mica has the property of splitting into thin sheets. It opens like the leaves of a book. A "white" (actually colourless), an amber, and a black variety are common. The formula for the white variety is $KH_2Al_3SiO_4$. Mica is produced in many places and is a valuable industrial material because it resists heat and is an excellent insulator. It is used as an electric insulator, for windows, in small house-heating stoves, in eye protectors, and for peep holes in furnaces and ovens. Ground mica is used as "Christmas tree snow," as a filler in some types of rubber goods, for dusting automobile tires, roofing materials, and asphalt shingles.

Courtesy of General Electric Co. Ltd.

FIG. 234
AN ELECTRIC INSULATOR

Mica is used in their manufacture.

Diatomaceous earth is the name given to the powdery aggregate of the siliceous support of minute plants known as *diatoms*. Diatomaceous earth (kieselguhr) is very porous; it is used as a filtering agent, as a thermal insulator, and as a porous medium to contain the nitro-glycerine of dynamite. Diatomaceous earth is also used in the manufacture of soaps, cosmetics, waxes, toothpastes, and printing inks. It is a delicate abrasive, and so it is the chief component of many of the best polishing and cleaning materials.

2. Preparation of Silicon

Silicon is prepared in industry by heating sand (SiO_2) with coke in an electric furnace. In this process it is necessary to make sure that there is not too much coke, because carborundum will be formed instead of pure silicon if there is an excess of carbon.

$$SiO_2 + 2\ C \longrightarrow Si + 2\ CO \uparrow$$

Silicon, when prepared in the electric furnace in this way, is a grey, *crystalline* substance. At ordinary temperatures, silicon is an inactive element, and it is very much like carbon in its chemical properties. If silicon is heated to a high temperature, it reacts with oxygen and a number of other elements, such as carbon, nitrogen, and some of the metals. Compounds, such as silicon carbide, SiC, which has the trade name of *carborundum*, and calcium carbide, CaC_2 (see page 286) are produced com-

Courtesy of Norton Co. of Canada, Limited

FIG. 235—MOST OF THE SILICON CARBIDE (CARBORUNDUM IS MADE INTO SHARPENING STONES AND GRINDING WHEELS. THE ABOVE PICTURE SHOWS A CYLINDRICAL SHAFT BEING GROUND BY AN ABRASIVE WHEEL MADE FROM CARBORUNDUM

mercially in the electric furnace, which can only be used where there is a cheap and plentiful supply of electrical energy. An alloy of iron and silicon, known as *ferrosilicon*, is produced when a mixture of ferric oxide (Fe_2O_3), sand, and coke is heated in an electric furnace. Ferrosilicon is used in the production of steel to introduce the amount of silicon required in the steel.

3. Silicic Acid and the Soluble Silicates

Most silicates do not react with strong acids. However, if a strong acid is added to a solution of a soluble silicate, such as sodium silicate, Na_4SiO_4, a jelly-like precipitate, known as orthosilicic acid, is formed. The equation usually given for this reaction is

$$Na_4SiO_4 + 4\ HCl \longrightarrow H_4SiO_4\downarrow + 4\ NaCl$$

Silicic acid is an extremely weak acid as it ionizes to a very slight extent. When this acid is heated, water and silicon dioxide are formed.

$$H_4SiO_4 \longrightarrow SiO_2 + 2\ H_2O$$

Most silicates do not dissolve in water, and only those of potassium and sodium are soluble. These soluble silicates can be prepared by heating a mixture of sand (SiO_2) and either the solid hydroxide or carbonate of the metal until the liquid state is obtained.

$$SiO_2 + Na_2CO_3 \longrightarrow Na_2SiO_3 + CO_2\uparrow$$
$$SiO_2 + 2\ NaOH \longrightarrow Na_2SiO_3 + H_2O$$

A concentrated water solution of sodium silicate is used in commerce under the name of *water glass*. This material has a number of industrial uses. It is used in certain types of soaps as a filler and to fire-proof fabrics which are to be used to make stage scenery in the theatre. Water glass is also used to waterproof cloth and wood and to keep eggs from spoiling. The water glass serves as a protective coating on the shell of the egg, preventing air from getting into the egg. Much is used as an adhesive, especially in the manufacture of cardboard cartons used for shipping purposes. Water glass is also used in making china cement, and as a binding material in the production of certain kinds of artificial stone.

4. Glass

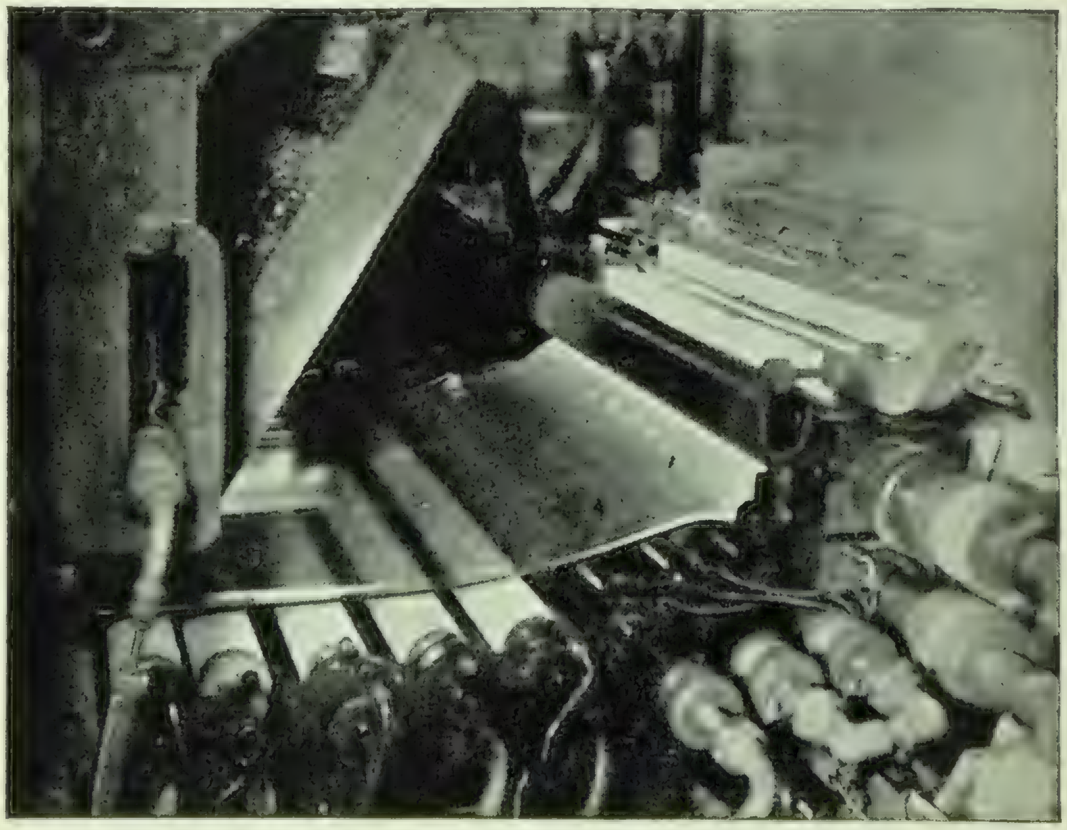
When cooled rapidly from the melt, silicates have a tendency to form glasses which are not crystallized. If cooled slowly, they would be crystalline and opaque.

Historians tell us that the Egyptians discovered how to make glass. The production of glass on a large scale started in Egypt about 1370 B.C. Sodium carbonate (Na_2CO_3) was melted with crushed quartz (SiO_2), limestone ($CaCO_3$) and copper compounds in crucibles to produce a blue glass. Glass made in Egypt was shipped to all parts of the Roman Empire.

Chemists have shown the modern manufacturer how to produce many new and useful kinds of glass. Ordinary glass, which is composed of *soda* (either sodium carbonate, Na_2CO_3, or sodium sulphate, Na_2SO_4), *limestone*, $CaCO_3$, and *sand*, SiO_2, cracks readily when suddenly heated or cooled too far. If common glass is heated strongly, it softens, and vessels made from it change their shape.

Pyrex glass is produced by replacing nearly all the calcium with boron (about 12 per cent B_2O_3). In addition, it contains more aluminum than other types of glass (about two per cent as Al_2O_3). Pyrex glass is strong and stands changes in temperature so well that cooking dishes can be manufactured from it.

Plate glass is made in somewhat the same way as a pie crust. A huge ladle, containing about half a ton of glass, pours it while



Courtesy of Messrs. Chance Bros. & Co. Ltd., Smethwick

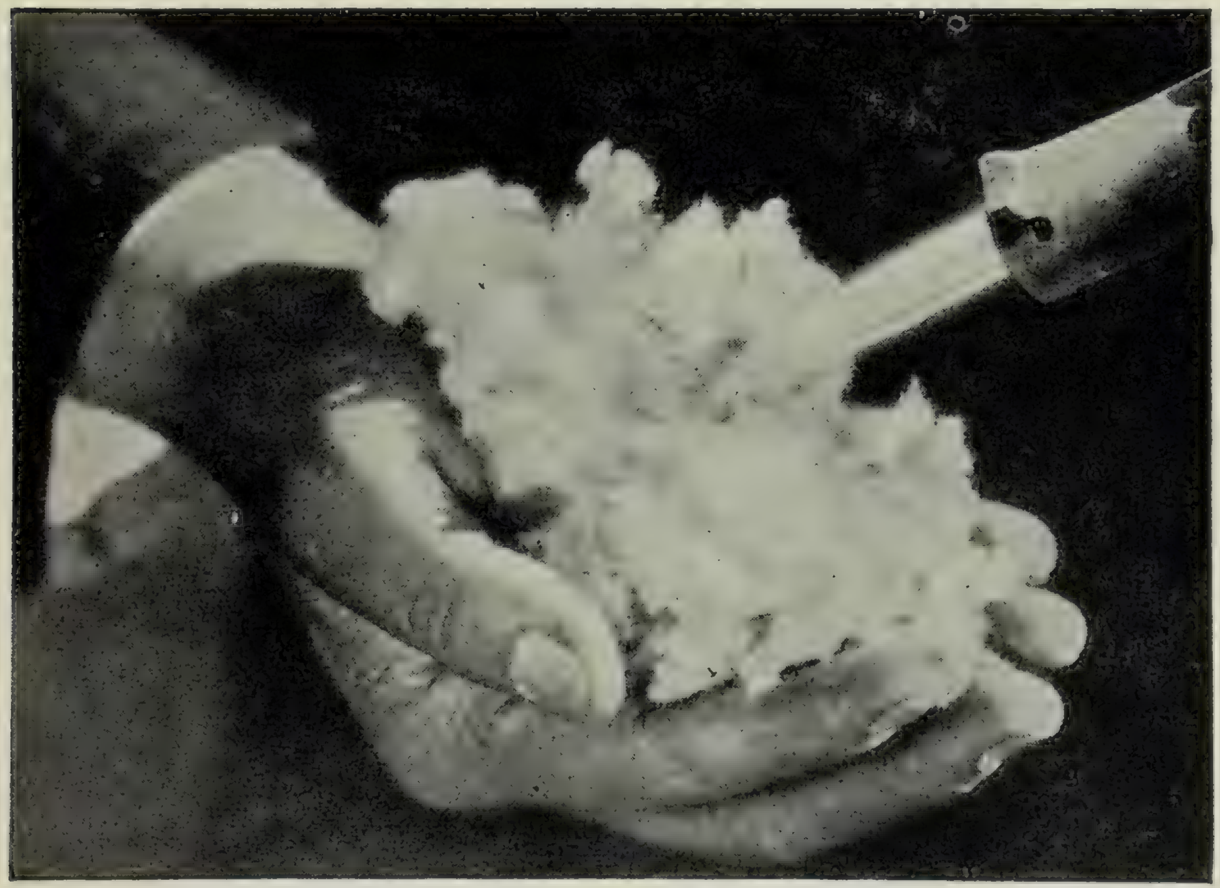
FIG. 236—THE MECHANICAL PRODUCTION OF ROOFING GLASS

The glass flows over a weir from the furnace and passes through the rollers.

red hot on an iron table, where it is rolled out to one-half inch thickness. The next part of the process consists of cooling the glass slowly and then grinding it to about one-quarter inch thickness with sand and rouge until it shines with the polish we observe in the plate glass windows of stores.

Optical glass for lenses of all kinds is produced by adding lead oxide to the glass mixture. Optical glass should be free of all colour producing materials and should also be free even from very small air bubbles or stringy waves. Cheap imitations of gems are made from glass very rich in lead (paste), and the glass of which cut-glass vessels are made is of this same kind but it contains less lead.

Shatter-proof glass is produced by cementing sheets of glass together in layers (usually two or three) with plastics. It is tough and strong. This type of glass does not splinter when broken but forms small comparatively harmless fragments. This toughened glass is about five times as strong as ordinary plate glass.



Courtesy of Canadian Johns-Manville Co. Ltd

Fig. 237—Even the Heat from a Blow Torch Will Not Cause Rock Wool to Burn—and the Heat is Not Conducted to the Hand. Rock Wool is Used for Insulation in the Walls of Dwellings

Recently a new form of glass, full of thousands of tiny air holes, has been produced. It is called *foamglas*. There are about 3000 air holes in one cubic inch of this type of glass, and it floats high in the water, having a density of 0.17. This spongy glass is used for life rafts, life belts, fish net floats, and in factory walls for insulation against heat. It is interesting to know that foamglas occurs in nature as pumice.

Another new type of glass is *fibrous glass*, which glass is in tiny filaments, as fine as cotton or wool fibres. This kind of glass is known as *fiberglas*. It comes in two forms, *glass wool*, and *glass thread*. *Rock wool* is quite similar to glass wool, but the materials used for its production are of a lesser degree of purity than those used in the manufacture of glass. Rock wool is used for insulation in the walls of dwellings. An important use of glass wool is for insulation against the flow of heat. For example, blankets of glass wool are wrapped around pipes which carry hot water or steam in large factories. The chief use of cloth woven from the long, thin yarns of glass is for electrical insulation, glass being one of the best electrical insulators. Glass threads are very strong and sometimes they are twisted into cables which are capable of holding up enormous weights.

5. Portland Cement

Portland cement consists of a mixture of complex silicates and aluminates of calcium; it has the property of hardening in either air or under water. It is made by grinding together the minerals required to make a good cement. Sometimes a natural limestone ($CaCO_3$) may contain enough silicates and aluminates to be satisfactory without the addition of clay. In other localities one part of clay must be mixed with four to five parts of limestone to give a satisfactory cement mix. The components may be ground dry or with water (wet process) to form "slurry."

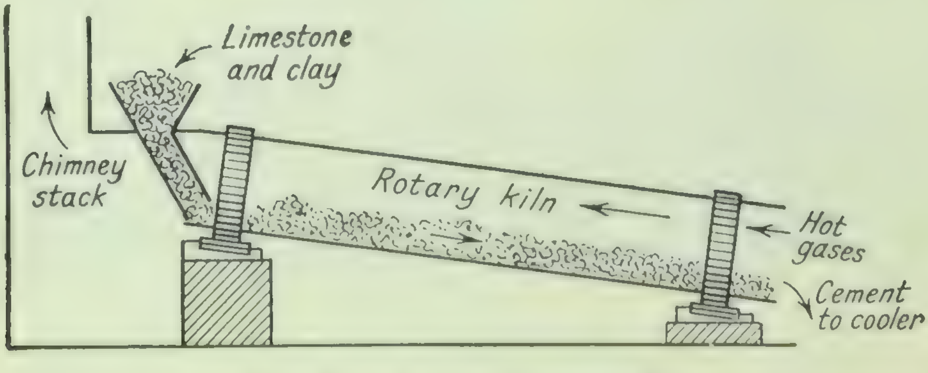


FIG. 238—ROTARY CEMENT KILN

The dry mixture, or "slurry," is heated from 1450° to 1500° C. (2642°-2732° F.) in a huge rotary kiln, as shown in Fig. 238, to produce a clinker.

The rotary furnace (kiln) is constructed of steel; it is about 12 feet in diameter, from 300 to 400 feet in length, and lined with heat-resistant brick. The finely ground raw materials are introduced at the upper end of the kiln, and the slow rotation of the kiln, which is inclined slightly downward, causes the mixture to move from the upper (cool) end to the lower (hot) end. At the lower end, the fuel is introduced and a flame is formed by the burning of oil, gas, or powdered coal, forced into the furnace under high pressure with the correct proportion of air to make sure that complete combustion takes place. By this method of heating, temperatures much higher than those needed to melt steel, glass, or aluminum are obtained. The substance in the furnace at the lower end is just below its melting point and forms itself into rounded balls, varying in diameter from one-eighth of an inch to over one inch. These balls are known as the clinker. They are allowed to drop from the lower end of the kiln into a cooler. After cooling the clinker is ground to a very fine powder and during this grinding operation a small amount (2 to 3 per cent) of gypsum ($CaSO_4 . 2\ H_2O$) is added to slow up the setting of the cement. The product formed by the above process is known as *Portland cement.*

There is no definite composition for Portland cement, and so we cannot write a chemical formula for it. However, it has been shown that the composition must be within certain definite limits. The composition of a typical cement is approximately as follows:

	Per cent
CaO	64
SiO_2	22
Al_2O_3	6
Fe_2O_3	3.5
MgO	2.5
SO_3, TiO_2, Na_2O, K_2O	2

The chief use of cement is for making concrete. Concrete is the substance produced when cement is mixed with water, sand and gravel, and allowed to set. Of course, different amounts of these materials are used, and the proportions depend upon the use of the concrete.

At the present time, about 10,000,000 barrels of cement are produced every year in Canada and this is a good index of building activity. The raw materials required to manufacture it are readily available in all parts of Canada and so we find cement plants in every section of the country.

Saskatchewan has rich deposits of clays, limestones and sands and, due to the industry and initiative of the people in this province, these materials have been utilized to develop ceramics and related industries. Saskatchewan has, indeed, led the way in this field; the University of Saskatchewan established a department of ceramics some years ago.

Research work was started on Portland cement a number of years ago at the University of Saskatchewan by Dr. T. Thorvaldson, now head of the Department of Chemistry. He directed a long series of researches, sponsored by the National Research Council at Ottawa, on Portland cement. As a result of this work, Dr. Thorvaldson and his co-workers were able to suggest an improved type of Portland cement which was of great value not only to the people of Saskatchewan but also to the rest of Canada. In fact, their work has been of much assistance to engineers in all parts of the world.

BORON (B)

Boron is at the top of Group III of the periodic system. It has a valence of three, and it possesses the typical properties of a non-metallic element. Boron occurs in nature as *boric acid* and *borax*.

Boron, in the free state, can be prepared by the reduction of boric oxide with powdered magnesium.

$$B_2O_3 + 3\ Mg \longrightarrow 2\ B + 3\ MgO$$

It is an amorphous, dark-brown powder; it combines with both nitrogen and oxygen, when heated in air, to produce the nitride BN and the oxide B_2O_3.

$$2\ B + N_2 \longrightarrow 2\ BN$$
$$4\ B + 3\ O_2 \longrightarrow 2\ B_2O_3$$

The element has no practical uses.

Boric acid, H_3BO_3 (the ortho acid) is usually prepared in the laboratory by the action of stronger acids upon solutions of borax.

$$Na_2B_4O_7 + H_2SO_4 + 5\ H_2O \longrightarrow Na_2SO_4 + 4\ H_3BO_3$$

It comes out of solution as thin, white, flaky crystals which are smooth to the touch. Boric acid is only slightly soluble in cold water, four grams dissolving in 100 c.c. of water at 18° C. However, it is quite soluble in hot water, 34 grams dissolving in 100 c.c. of water at 100° C. Boron gives a green colour to a Bunsen flame. Boric acid is very slightly ionized, and so its solution has scarcely any effect on blue litmus paper. It is used in water solution as a mild antiseptic and is especially useful in this respect as an *eye wash.* It is also used as a preservative for foods.

Borax, sodium tetraborate, $Na_2B_4O_7 . 10\ H_2O$, is the most important compound of boron. Most of the world's supply of borax is obtained from desert regions in California.

Borax is derived from tetraboric acid $H_2B_4O_7$, which can be obtained by heating boric acid gently.

$$4\ H_3BO_3 \longrightarrow H_2B_4O_7 + 5\ H_2O$$

Since borax is decomposed slightly by water (hydrolysis), its water solutions are basic to litmus. This fact makes it useful as a *cleansing agent;* it is often found in the harsher kinds of soaps.

For the same reason, borax is used to a considerable extent as a *water softener.* It is also used in the production of certain kinds of *glass*, such as pyrex, as well as in the manufacture of *glazes* and *enamels* for metal ware and pottery. Since borax, when melted, dissolves metallic oxides, it is used in *soldering* and *welding* to remove the undesirable metallic oxides from the surface to be soldered or welded.

When borax is heated, it melts to form a clear glass. The oxides of certain metals give characteristic colours to beads of borax, which act as a flux dissolving the metallic oxide. This is done in the laboratory by bringing the loop of a red hot platinum wire into contact with some borax, and then heating strongly in the tip of a Bunsen flame. After a minute or two the borax shrinks into a transparent bead. The bead is then dipped into a saturated solution of some metallic compound, such as cobalt nitrate, and heated again in the outer portion of the Bunsen flame (oxidizing) until the colour is uniform. Cobalt turns the bead deep blue. The colours obtained by using various metallic ions are given in Table 31. The test is known as the *borax bead test for metals.* The chemical reaction involved in this test can be understood if we write the formula for borax as $(NaBO_2)_2 . B_2O_3$.

For example, with cupric oxide, CuO, the following equation represents the reaction which takes place:

$$(NaBO_2)_2.B_2O_3 + CuO \longrightarrow \underset{\text{(sodium metaborate)}}{2\ NaBO_2} + \underset{\text{(cupric metaborate)}}{Cu(BO_2)_2}$$

It is important to remember that, for any given metallic ion, the colour of the bead may depend on whether one uses an *oxidizing* or a *reducing flame* when fusing the material being tested into the bead.

TABLE 31—THE COLOUR OF BORAX BEADS WITH SOME METALLIC IONS

Metallic Ion	Oxidizing Flame	Reducing Flame
Chromium	green	green
Cobalt	blue	blue
Copper	blue	red
Iron	yellow	green
Manganese	violet	grey
Nickel	brown	grey

EXERCISES

1. (a) Why is silicon such an important element?
   (b) What is a mineral?
   (c) What is a rock?
2. Write a short note on silicon dioxide.
3. Write a short note on silica glass.
4. (a) What is a silicate?
   (b) Write a brief note on feldspar.
   (c) Discuss the following topics briefly: talc, the clay minerals, asbestos and mica.
5. (a) What are diatoms?
   (b) Write a note on the uses of diatomaceous earth.
6. (a) How is free silicon obtained?
   (b) Write the equation to represent the reaction in (a).
   (c) What is ferrosilicon and what is its chief use?
7. (a) How is silicic acid prepared in the laboratory?
   (b) Write the equation for the reaction in (a).
   (c) How can pure sand be prepared in the laboratory? Write the equation for the reaction.
8. (a) What is water glass?
   (b) Write a note on the uses of water glass.
9. (a) What is glass?
   (b) Write short notes on the following: pyrex glass, optical glass, plate glass, foamglass and fiberglas.

10. (a) What is Portland cement?
    (b) Write a note on the manufacture of Portland cement.
    (c) What is concrete?
11. (a) Write the equation for the preparation of free boron.
    (b) How is boric acid prepared in the laboratory? Write the equation for the reaction involved.
12. (a) What is borax?
    (b) Tabulate five uses of borax.
    (c) Describe carefully the borax bead test for metals.

CHAPTER LVII

COPPER, SILVER AND GOLD

Interesting examples of the practical applications of chemistry to everyday life may be found in the production and use of metals. The metals known to the ancients were gold, silver, copper, lead, tin and mercury. Gold and copper have been used since prehistoric times, and it is likely that these were the first metals used by man. Until the middle of the nineteenth century the only metals in common use were copper, iron, tin, zinc and the mixtures or alloys called bronze (copper and tin) and brass (copper and zinc).

Modern chemists are interested in some 70 metals and metallurgists use more than 30 of them in the production of our present day alloys, such as steels, bronzes and babbits. Canada is fortunate in having rich deposits of most of the important metals. Many of these deposits are found in the Laurentian Shield. This country is the chief producer of nickel, platinum and radium, and is among the leaders in the production of copper, lead, zinc, aluminum, magnesium, cobalt and silver.

There are various ways of grouping the metals. For example, metals could be grouped into the heavy metals and the light metals. They could also be classified on the basis of their melting points. Metals with high melting points could be grouped together and those with low melting points could be put in another class. However, chemists usually group the metals according to their position in the Periodic Table, and this plan will be followed here. Copper, silver and gold are found in Group I of the Periodic Table, so they will be considered first. Some metals in Group II will be discussed next, and so forth until Group VIII is reached.

COPPER (Cu)

1. Occurrence

Copper is the second most important metal. The common use of electricity in modern times has greatly increased the demand for copper. The annual world production of this metal is more than two million tons. Due to its low rate of chemical activity and to the fact that it is often found in the free state, copper has been used by man from the earliest times. In the days of the Romans it was obtained from the island of Cyprus, and was given the Latin name of "cuprum," from which the symbol "Cu" is derived.

Copper ores are quite widely distributed in nature, and many countries have more or less abundant deposits. *Free* or *native copper* occurs in northern Michigan. The best ores are the various forms of the sulphides, such as *chalcopyrite*, $CuFeS_2$, *bornite*, Cu_3FeS_3, and *chalcocite*, Cu_2S, which are present in the Montana and Arizona deposits. The lower oxide, *cuprite*, Cu_2O, a red mineral, is an excellent ore, occurring in South America. Another ore of copper is *malachite*, $CuCO_3 . Cu(OH)_2$, a green mineral, which is sometimes polished and used as an ornamental stone.

2. Metallurgy

There are two chief methods of securing free copper from its ores, the *leaching process* and the *smelting process*. These two methods will now be considered briefly.

(1) The Leaching Process. This method can be used only if the ore is an *oxide* or a *carbonate*. In this process the ore is treated with dilute sulphuric acid and the copper compound is converted to the soluble copper sulphate.

$$CuCO_3 + H_2SO \longrightarrow CuSO_4 + H_2O + CO_2\uparrow$$

The free copper is obtained by electrolysis of the copper sulphate solution.

(2) Smelting Process. This is the important method used to obtain free copper from the sulphide ores. The chief steps are:

(a) *Concentration of Ore*. It is necessary to concentrate low grade ores. This is done by a relatively new mining process, known as flotation. In this process the ore is mixed with water containing a small amount of pine oil. The mixture is agitated by a rapid stream of air and an oily foam is formed on the surface. The copper sulphide particles are *adsorbed* by this foam. The earthy particles are not attracted to the foam and they settle to the bottom. The foam, along with the copper sulphide, is removed and separated from the mineral by distillation.

(b) *Roasting*. This stage of the process removes volatile oxides such as arsenic oxide, antimony oxide, and part of the sulphur and sulphur dioxide.

(c) *Formation of Matte.* The ore is next mixed with silica (SiO_2) and limestone ($CaCO_3$) and heated in a blast furnace. The matte is a mixture of molten cuprous and ferrous sulphides ($Cu_2S + FeS$), with certain impurities such as silver and gold.

(d) *Blister Copper.* The copper matte is poured into a special Bessemer converter where it is reduced to free copper. The blister copper still contains impurities, such as silver and gold.

(e) *Electrolytic Refining.* Blister copper is refined by electrolysis (see page 274) until it is about 99.97 per cent pure.

3. Physical Properties

(1) Copper possesses a characteristic reddish colour.
(2) It is a heavy metal, having a density of 8.92.
(3) This metal is very malleable and ductile.
(4) Copper is a good conductor of heat and electricity (next to silver in these properties).
(5) It melts at 1083° C. and boils at 2300° C.

4. Chemical Properties

(1) Copper is oxidized slowly in moist air containing carbon dioxide. A green basic carbonate is formed and this compound serves as a protective coating to prevent further corrosion of the metal.

$$2\,Cu + O_2 + CO_2 + H_2O \longrightarrow CuCO_3 . Cu(OH)_2$$

Bronze statues and copper roofs become green in colour due to the formation of this basic carbonate.

(2) Copper is below hydrogen in the electromotive series of the metals, and so dilute hydrochloric and dilute sulphuric acids have very little effect on copper.

(3) It reacts with nitric acid and hot concentrated acids. These acids are oxidizing agents and the metal is attacked by them to produce gases other than hydrogen:

$$3\,Cu + 8\,\underset{\text{(dilute)}}{HNO_3} \longrightarrow 3\,Cu(NO_3)_2 + 4\,H_2O + 2\,\underset{\text{(nitric oxide)}}{NO\uparrow}$$

$$Cu + 4\,\underset{\text{(concentrated)}}{HNO_3} \longrightarrow Cu(NO_3)_2 + 2\,\underset{\substack{\text{(nitrogen}\\\text{dioxide)}}}{NO_2\uparrow} + 2\,H_2O$$

$$Cu + 2\,\underset{\text{(concentrated)}}{H_2SO_4} \longrightarrow CuSO_4 + SO_2\uparrow + 2\,H_2O$$

(4) When copper is heated, it combined directly with oxygen, sulphur, and the halogens.

$$2\,Cu + O_2 \longrightarrow 2\,CuO$$
$$Cu + S \longrightarrow CuS$$
$$Cu + Cl_2 \longrightarrow CuCl_2$$

5. Uses

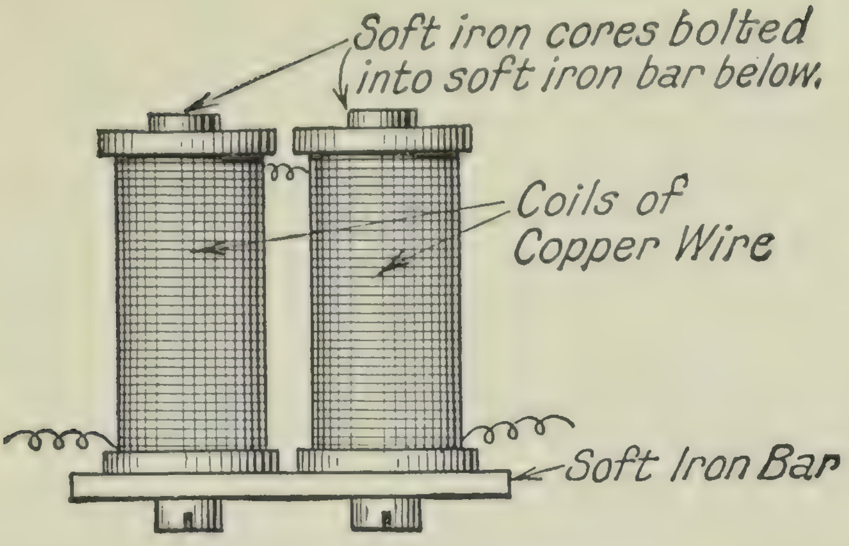


FIG. 239—AN ELECTROMAGNET
Much *copper* is required in its construction.

(1) The greatest use of copper is as an electrical conductor and for this purpose it must be very pure. Impurities lower the conductivity to a marked degree: for example, .03 per cent of arsenic lowers the conductivity as much as 14 per cent.
(2) Much copper is used as a roofing material.
(3) It is used extensively in making kettles, stills, evaporating pans, and boilers.
(4) Copper is used in making plates for printing and illustrating books.
(5) This metal is also used to sheathe wooden ships.
(6) Much copper is used in the production of over 1000 different alloys: for example, there are about 300 different varieties of brass (copper and zinc). Bronze is an alloy of copper and tin, and there are aluminum bronzes, consisting of copper and aluminum.
(7) Another important use of copper is in the production of *coinage.* The one cent pieces (coppers) consist of about 95 per cent copper, three per cent tin, and two per cent zinc. Gold and silver coins contain about ten per cent copper, and nickel coins are made up of about 75 per cent copper and 25 per cent nickel.

6. Copper Compounds

Copper produces two series of salts: *cuprous*, in which copper has a valence of *one;* and *cupric* in which it has a valence of *two*. Cuprous oxide, Cu_2O, is an example of a compound in which the valence of copper is one. *Cupric oxide*, CuO, is an illustration of a compound in which the valence is two.

Copper sulphate, $CuSO_4.5H_2O$, also known as *blue vitriol* or *bluestone* in the crystalline form, is the most important copper salt. It is made by the action of air and warm, dilute sulphuric acid on copper:

$$2\ Cu + O_2 + 2\ H_2SO_4 \longrightarrow 2\ CuSO_4 + 2\ H_2O$$

The anhydrous copper sulphate, $CuSO_4$, is prepared by heating the blue crystals. Bluestone crystals show the property of efflorescence in dry air. When copper sulphate is dissolved in water, it hydrolyzes slightly, producing an acid reaction. Copper sulphate is used in gravity batteries (Daniell cells), in copper refining, in electrotyping, and in calico printing. Minute plant organisms, known as algae, give water a very disagreeable taste. These organisms can be destroyed by adding a small amount of copper sulphate to the water. Bordeaux mixture, consisting of copper sulphate mixed with calcium hydroxide is used as a *fungicide.* Copper sulphate is also used to prepare other copper compounds such as Fehling's solution.

7. Test for Cupric Ions

The best known test for cupric ions is to add an excess of ammonium hydroxide to the solution believed to contain cupric ions. The presence of cupric ions is indicated by the formation of an intense blue colour, which is due to the formation of the cupric-ammonia ion, $Cu(NH_3)_4^{++}$. Ionic equations for the formation of this ion, when an excess of ammonium hydroxide is added to the cupric sulphate, are shown below.

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$

$$\begin{tikzcd}
4\,NH_4OH \arrow[r, shift left] \arrow[r, leftarrow, shift right] & 4\,NH_3 \arrow[d, shift left] \arrow[d, leftarrow, shift right] & +\ 4\,H_2O \\
 & Cu(NH_3)_4^{++} & \\
 & \text{(cupric-ammonia ion)} &
\end{tikzcd}$$

The cupric-ammonia ion is an example of a complex ion and other complex ions are formed by other metallic ions, such as silver or zinc.

SILVER (Ag)

1. Occurrence

Silver, the most common of the precious metals, is found in the free state in Canada at Cobalt, Ontario. Its most valuable ore is the sulphide, Ag_2S, known as *argentite.* A large amount of the silver which is produced comes from the refining of copper, lead, and nickel, since Ag_2S is often mixed in small amounts with the sulphides of these metals. Mexico is the largest producer of silver, producing about twice as much as the United States, which ranks second. Canada and South America also produce considerable quantities.

2. Properties

Silver is a soft, white metal which can take a very high polish. It is the most ductile and malleable metal next to gold. Silver is better than all other metals as a conductor of heat and electricity. This metal is not attacked by oxygen, but sulphur compounds tarnish it due to the formation of silver sulphide.

3. Uses

Silver is used extensively in the manufacture of *jewelry* and as a coating on *silver-plated ware.* British *coins* contain 92.5 per cent silver (Sterling silver). Much silver is used in plating *mirrors* due to its property of reflecting light so well. Silver, alloyed with mercury is used as a dental amalgam. *Silver vessels* also find many uses in certain food industries.

4. Silver Nitrate, $AgNO_3$

Silver nitrate, also known as *lunar caustic,* is the most important silver compound. It is prepared by the reaction of dilute nitric acid on silver.

$$3\ Ag + 4\ HNO_3 \longrightarrow 3\ AgNO_3 + 2\ H_2O + NO\uparrow$$

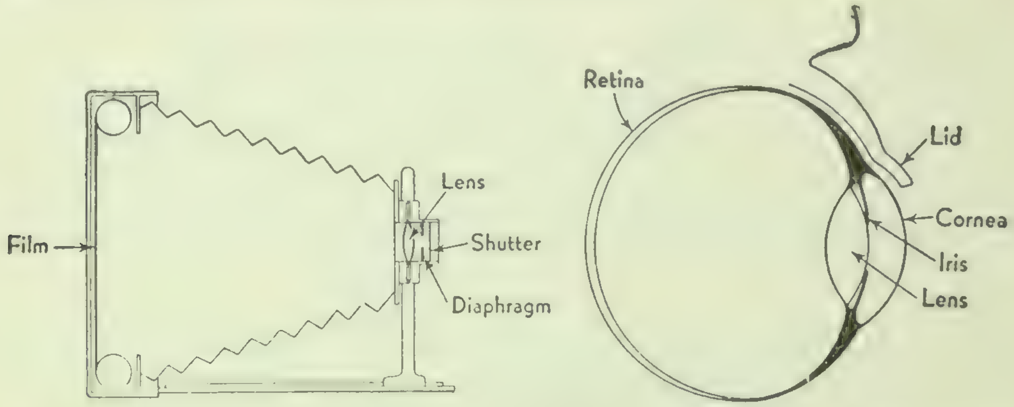
Silver nitrate is used to make other compounds of silver and to cauterize wounds. AgCl, AgBr, and AgI are known as the silver halides; they are very sensitive to light. Vast amounts of these substances, especially the bromide, are used annually by the photographic industry.

5. Photography

Photography enables man to preserve a world of events by means of pictures. Besides being an interesting hobby, it is of great practical use and has become a valuable scientific tool. Many important advances in science (of recent years) have been aided by the application of photography to record the phenomena studied.

Taking a photograph usually involves the making of two pictures, the *negative* and the *print.* The negative is usually made on a supporting sheet of glass or celluloid. The print or finished picture is made on paper.

The supporting celluloid, or glass plate, is covered with a layer of gelatin emulsion in which there are colloidal particles of silver bromide (AgBr) and silver iodide (AgI). In negatives these particles may vary from eight to twelve one hundred thousandths of an inch in diameter. For prints, however, the particles are about one-fourth this size.



Courtesy of Canadian Westinghouse Co. Ltd.

FIG. 240—THE CAMERA AND THE EYE ARE SIMILAR IN PRINCIPLE. THE SHUTTER CORRESPONDS TO THE LID, THE DIAPHRAGM TO THE IRIS, THE LENS TO THE LENS OF THE EYE, THE FILM TO THE RETINA

When the plate or film so prepared is placed in the back of a camera and the image of some object is focused upon it, the silver bromide undergoes a complicated change which depends on the exposure. Too long or too short an exposure will prevent us from obtaining the proper contrast of light and shade. In other words, the degree of decomposition at any one place on the film varies with the intensity of the light. The reaction may be expressed in a simple way as follows:

$$AgBr \longrightarrow Ag + Br$$

In this way an image of the object photographed is produced upon the plate. This image, however, is invisible and is, therefore, called latent. It can be made visible by the process of developing.

To develop the image the exposed plate is immersed in a solution called the *developer*, which consists of a reducing agent. The developer changes the silver compounds on which light has acted into very small particles of free silver, but it will not (within a reasonable time) change those in which action has not been started by the light. The silver so formed is deposited in the form of a black film which sticks closely to the plate. It is these black particles of silver which make up the dark part of the picture. The silver compounds which were not immediately acted on by the developer must be removed, otherwise they will be changed to silver and the picture ruined.

To remove the unchanged silver compounds the developed picture is placed in a *fixing bath,* which consists of a solution of sodium thiosulphate ($Na_2S_2O_3$) or "hypo." The unchanged silver salts in the gelatin dissolve in the fixing solution. The plate is then washed with water and dried. The plate is now called the *negative* because whatever in the original was bright is represented by dark silver and where the original was dark the negative has been washed clear.

The print is made on paper which is prepared in almost the same way as the negative plate. The negative is placed upon this paper and exposed to the light so that the light must pass through the negative before striking the paper. The least light comes through where the negative is darkest; this part will be the lightest part of the picture when the silver bromide has been dissolved out. Light passes through the lighter parts of the negative and strikes the sensitive silver bromide on the paper; this part on developing will be dark. Thus, the print is the reverse of the negative, and as the light and shade correspond with the original, it is called a *positive.* The tint of the positive is sometimes changed by a process called toning.

GOLD (Au)

1. Occurrence

The use of gold dates from earliest times. It is probable that it was one of the first metals used by man. Native gold occurs in veins running through quartz rock and in the beds of streams whose sands have been formed from the breaking down of such gold-bearing quartz. It has been discovered in nuggets which vary in size from a tiny pebble to a mass weighing over 100 pounds. South Africa, Western Australia, Russia, Canada and the United States are the gold producing countries of the world.

2. Metallurgy

Native gold is obtained in crude form by placer mining. The sand containing the gold is shaken or stirred in troughs of running water, called sluices. The sand is swept away leaving the heavier gold at the bottom of the sluice. Sometimes the sand containing the gold is washed away from its natural location into the sluices by powerful streams of water delivered under pressure from pipes. This method of securing gold is called hydraulic mining. In vein mining the gold-bearing quartz is stamped into fine powder in stamping mills, and the gold is extracted by either the amalgamation or the cyanide process.

In the amalgamation process the powder containing the gold is washed over copper plates whose surfaces have been amalgamated with mercury. The gold sticks to the mercury or alloys with it, and after a time the gold and mercury are scraped off and the mixture is distilled. In the distillation process the mercury comes off as a vapour, leaving the gold behind in the retort ready for refining.

The cyanide process depends upon the fact that gold is soluble in a solution of sodium cyanide (NaCN) in the presence of the oxygen of the air.

$$4\ Au + 8\ NaCN + O_2 + 2\ H_2O \longrightarrow 4\ NaAu(CN)_2 + 4\ NaOH$$

The powder from the stamping mills is treated with a very dilute sodium cyanide solution which dissolves the gold according to the above equation. The gold is obtained from this solution by electrolysis.

3. Properties

Gold is a yellow metal having a density of 19.3. It is the most malleable and ductile of all the metals. Gold has been hammered out into sheets so thin that it requires 280,000 leaves placed one upon another to occupy the thickness of an inch. A further illustration of the great malleability of this metal is that one ounce can be hammered out so as to cover 189 square feet. Gold is very ductile as shown by the fact that one ounce can be drawn into a wire about 50 miles long. Gold is not attacked by air or the common acids, but it is dissolved by aqua regia. Gold reacts with the chlorine formed in aqua regia to produce auric chloride, $AuCl_3$.

4. Uses

Pure gold is used as *gold leaf*. The metal is too soft to be used alone for other purposes and is alloyed with silver or copper. The fineness of gold is usually expressed in terms of carats, 24 carat gold being pure, while 18 carat (75 per cent) is the grade used for the best *jewelry*. When gold is used for *coins*, it is alloyed with copper to give it hardness. British coins contain 92.5 per cent gold (22 carat).

EXERCISES

1. Discuss copper under: (a) occurrence; (b) metallurgy; (c) physical properties; (d) chemical properties; (e) uses.
2. (a) What is the difference between a cuprous salt and a cupric salt?
   (b) Write the formulas for the following: cuprous oxide, cupric oxide, cuprous chloride, cupric chloride, cuprous sulphide and cupric sulphide.
3. (a) Write a note on blue vitriol.
   (b) What is Bordeaux mixture?
   (c) What is the test for the cupric ion?
   (d) What is a complex ion?
   (e) Give one example of such an ion.
4. Discuss silver under: (a) occurrence; (b) properties; (c) uses.
5. Write a note on lunar caustic.
6. Write a short essay on photography under: (1) exposing; (2) developing; (3) fixing; (4) printing.
7. Discuss gold under: (a) occurrence; (b) metallurgy; (c) properties; (d) uses.

Chapter LVIII

SOME OTHER IMPORTANT METALS

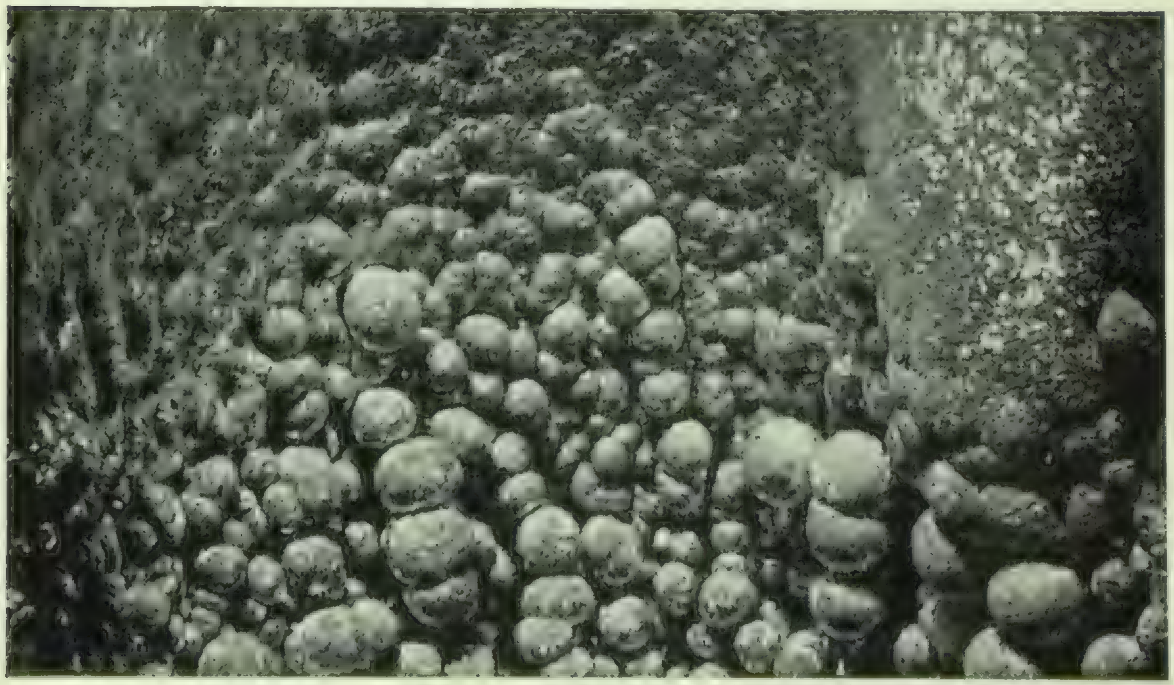
MAGNESIUM, ZINC, CADMIUM, AND MERCURY

(Some Group II Metals)

MAGNESIUM (Mg)

Magnesium is one of the most abundant metals present in the earth's crust, but it is found in compounds from which it is difficult to obtain the metal. The extraction of magnesium metal from sea water is one of the outstanding scientific achievements of the past few years. The production of this metal from Canadian dolomite ($CaCO_3 . MgCO_3$) ranks as an important development in the field of metallurgy. The dolomite process was developed in the National Research Council laboratories by Dr. Lloyd M. Pidgeon, and it is sometimes known as the *ferro-silicon method.* Ferro-silicon, made at Beauharnois, Quebec, is the reducing agent. Silica (SiO_2) is produced in the process and combines with the lime (CaO) present in the calcined dolomite to form dicalcium silicate, $(CaO)_2 . SiO_2$, which is not volatile. The magnesium is liberated according to the following equation.

$$2\ (MgO + CaO) + Si \longrightarrow 2\ Mg\uparrow + (CaO)_2.SiO_2$$



Courtesy of Canadian Industries, Ltd.

Fig. 241—Magnesium Produced by the Pidgeon Process is Deposited as a Ring of Great Purity, Each Tiny Crystal Shining Like a Diamond

The reaction takes place in a vacuum. The magnesium is volatilized and is condensed as a ring or crown of great purity.

Magnesium is very useful because of its lightness, which makes it valuable as a construction material for aircraft. It is also used in the manufacture of fireworks, flashlight powders, and light alloys, such as magnalium, which is made up of magnesium and aluminum. It has been found that a small amount of manganese and zinc improves the resistance of magnesium to corrosion. For example, a typical magnesium alloy of this type consists of: aluminum, five per cent; zinc, three per cent; manganese, 0.15 per cent; and magnesium, 91.85 per cent. When alloyed in this way, magnesium can be handled like steel. It can be rolled into sheets, plates, and strips. It can also be cast or extruded as bars, rods or tubing. Such an alloy is very easy to machine. A sharp tool cuts it as a hot knife cuts butter, and it only weighs one-quarter as much as steel.

ZINC (Zn)

Zinc does not occur in the free state in nature. Its chief ore is zinc blende (ZnS). The first step in converting this ore into free zinc is to heat it in a current of air. This process is known as *roasting* and the sulphide is changed to the oxide according to the following equation.

$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2\uparrow$$

The zinc oxide is then reduced with coke in small clay retorts.

$$ZnO + C \longrightarrow Zn + CO$$

The heat, necessary to bring about the reduction, also converts the free zinc to a vapour. This vapour is then changed to a liquid by cooling, and permitted to solidify into ingots, called *spetter*.

Zinc behaves as a typical metal when it comes in contact with dilute acids, hydrogen being liberated.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$$

It may also act as a non-metal when it reacts with strong bases, producing compounds known as *zincates*.

$$Zn + 2\,NaOH \longrightarrow H_2\uparrow + \underset{\text{(sodium zincate)}}{Na_2ZnO_2}$$

Zinc burns in air to form zinc oxide.

$$2\,Zn + O_2 \longrightarrow 2\,ZnO$$

At ordinary temperatures, zinc corrodes only to a slight extent because of the formation of a protective coating of zinc carbonate.

Zinc is used for roofing, lining iron tanks, and as a protective coating on iron to prevent it from rusting. Iron, which has been protected in this way, is known as *galvanized* iron. Zinc is used in the printing business to produce plates for illustrations. It is also used to make the containers of dry cells (see page 290), and in the preparation of alloys, such as brass, bronze, and German silver.

CADMIUM (Cd)

Cadmium sometimes occurs in nature as the sulphide *greenockite*, CdS. However, it is generally found as an impurity in certain ores of zinc. For example, zinc blende always contains small quantities of cadmium and indium.

The cadmium can be separated from the zinc by distillation because of the difference in their boiling points (zinc boils at 929° C.; cadmium at 770° C.).

Cadmium is a white metal much more malleable than zinc. Like the other members of Group II of the Periodic Table, it has a valence of two. Its chief use has been in the making of *low melting alloys* for automatic fire sprinkler systems and fuses. It is used to a considerable extent in electro-plating steel to protect it from corrosion. Cadmium is also used to make bearing metals. Its sulphide, CdS, is used as a yellow pigment for paints.

MERCURY (Hg)

Mercury is the only common metal which exists in the liquid state at ordinary temperatures. Its chief ore is cinnabar (mercuric sulphide, HgS). Mercury is now produced in Canada from deposits in British Columbia. When cinnabar is roasted, the sulphur is oxidized to sulphur dioxide and the mercury is liberated as a vapour, which is condensed.

$$\mathbf{HgS + O_2 \longrightarrow Hg + SO_2\uparrow}$$

The properties of mercury make it especially suitable for use in thermometers, barometers and other scientific instruments. The alloys of this metal are known as *amalgams*. The dentist uses silver amalgam in filling teeth. Mercury shows two valences. It is monovalent in the *mercurous* compounds and divalent in the *mercuric* compounds. *Mercurous Chloride* (calomel, $HgCl$) is a good example of a compound in which mercury is monovalent. It is a white, insoluble solid used in medicine. *Mercuric* chloride ($HgCl_2$), also known as corrosive sublimate, is a good example of a mercuric salt. It is used as an antiseptic in medicine.

INDIUM (In)

(A Group III Metal)

Indium (In) is produced on a very small scale because this metal never occurs in an ore in an amount greater than a small fraction of one per cent. Acids and alkalies are used to separate it from other materials and this requires long and very careful operations. Since this metal is in Group III its valence is three. It is remarkable for its resistance to oxidation.

Cadmium bearings are covered with a thin plating of indium which increases their life and performance.

TITANIUM, TIN AND LEAD

(Some Group IV Metals)

TITANIUM (Ti)

Titanium is rather a common element in the earth's crust; it is considered to be tenth from the standpoint of abundance. Its chief ores are *ilmenite* (ferrous titanate), and *rutile*, TiO_2.

Titanium is very much like silicon in its chemical behaviour. Due to its great affinity for both oxygen and nitrogen, titanium is used in the making of steel to remove gases from the molten metal. An alloy of iron and titanium is very strong and has a high ability to stand up against much wear. Titanium dioxide, TiO_2, is used to a considerable extent in the paint industry as a body. It is sometimes known under the trade name of *titanox*. Titanium dioxide paints seem to remain white and resist attack by the weather longer than paints containing white lead.

TIN (Sn)

The chief ore of tin is *cassiterite*, stannic oxide, SnO_2. Free tin is secured by reduction with carbon.

$$SnO_2 + C \longrightarrow Sn + CO_2\uparrow$$

Tin is a silvery-white metal which is not attacked by ordinary corrosive substances; so tin is used chiefly as a protective coating for other metals. *Tin plate*, from which tin cans are manufactured, is made by dipping thin sheets of iron into molten tin. Tin is a component of many important alloys, such as bronze, pewter, solder, Babbit-metal, and type metal.

Tin is an element which shows variable valence, forming two series of compounds, *stannous* in which tin has a valence of two and *stannic* in which tin has a valence of four.

LEAD (Pb)

The chief ore of lead is *galena* (lead sulphide, PbS) of which rich deposits are found in British Columbia. Because most lead ores contain only from five to ten per cent lead they must be concentrated. This is usually done by the oil flotation process before the extraction of the metal can be started. The ore is then roasted until about two-thirds of the sulphide is changed to the oxide.

Courtesy of Canadian Industries, Ltd.

Fig. 242—The Largest Non-Ferrous Smelter in the World, the Consolidated Mining and Smelting Co. Plant at Trail, B.C. Produces 700 Tons of Lead Alone Each Day. It Also Produces Zinc, Sulphur, Gold, Silver, Bismuth and Tin

$$2\ PbS + 3\ O_2 \longrightarrow 2\ PbO + 2\ SO_2\uparrow$$

The air is now turned off and the heating carried on at a higher temperature. Lead is liberated by the reduction of the oxide formed at first by the remaining lead sulphide.

$$PbS + 2\ PbO \longrightarrow 3\ Pb + SO_2\uparrow$$

Lead is the heaviest of the common metals. It is quite soft and malleable. The melting point of this metal is 375.5° C. Lead is oxidized when exposed to air, changing from a bright lustre to a dull hue, and the protective coating formed in this way prevents further corrosion of the metal. The metal reacts readily with nitric and acetic acids, forming soluble salts. It is only slightly attacked by hydrochloric acid or dilute sulphuric acid.

The chief use of lead is in the manufacture of lead storage batteries. The next use, in order of importance, is for sheathing cable. Another important use for lead is in making white lead for paints. Lead is also used in the manufacture of water pipes, alloys and roofing materials. It is used to line the chambers used for the manufacture of sulphuric acid by the lead chamber process.

White lead is the most important compound of lead. It is a basic carbonate with the formula $Pb(OH)_2 . 2\ PbCO_3$. White lead has been made for many years by a process known as the *Dutch process*. In this process lead, acetic acid and carbon dioxide take part in a number of reactions to produce a heavy, white powder, which is used extensively as a *body* in the manufacture of paint. It requires about three months for this process to take place. Paints are always made up of two, and usually three components: the *vehicle*, the *body* and the *pigment*. Linseed oil is generally the vehicle; white lead is the usual body; and, if white paint is not wanted, some pigment must be added to produce the desired colour. These pigments are usually inorganic substances.

ARSENIC, ANTIMONY AND BISMUTH

(Some Group V Metals)

The elements arsenic, antimony and bismuth are members of Group V, sometimes known as the nitrogen group. Arsenic and antimony show amphoteric properties, but due to the fact that their oxides form acids, they are usually classed as non-metals. Bismuth oxide, on the other hand, produces a base when added to water, and so bismuth is classed as a metal. Many of the uses of arsenic and antimony emphasize the fact that these elements have desirable metallic properties; for this reason they should be dealt with, at least to a certain extent, from the metallic viewpoint.

ARSENIC (As)

The chief ore of arsenic is *arsenopyrite* or *mispickel*, FeAsS. Many natural sulphides, such as those of copper, iron or lead, contain traces of arsenic; therefore, much of the arsenic used in industry is obtained as a by-product from smelters.

Arsenic can be prepared by heating arsenopyrite, the element subliming away from the ore.

$$FeAsS + (heat) \longrightarrow FeS + As\uparrow$$

Arsenic is a steel-grey, crystalline, brittle solid. It burns in air, forming arsenic trioxide, As_2O_3.

$$4\ As + 3\ O_2 \longrightarrow 2\ As_2O_3$$

The metal combines directly with halogens, sulphur and many of the metals.

$$2\ As + 3\ Cl_2 \longrightarrow 2\ AsCl_3$$
$$3\ Zn + 2\ As \longrightarrow \underset{\text{(zinc arsenide)}}{Zn_3As_2}$$

Arsenic is a very poisonous substance, and the poisonous nature of all arsenic compounds makes them of great use as *insecticides.*

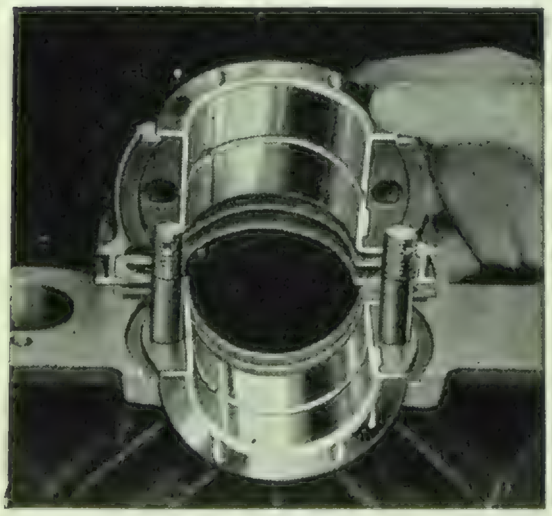
A small quantity of arsenic is used in making certain alloys. A small amount is also used in the production of lead shot; the arsenic causes the molten lead to harden rapidly.

ANTIMONY (Sb)

Antimony occurs in nature as a mineral *stibnite,* Sb_2S_3. It can be prepared by heating its sulphide with iron.

$$Sb_2S_3 + 3\ Fe \longrightarrow 3\ FeS + 2\ Sb$$

Antimony is a silvery, brittle, crystalline solid. It expands when it changes to the solid state, a property which makes it especially valuable in the preparation of type metal, which is an alloy of lead, tin and antimony. *Babbit-metal* (Sb, Pb, Sn, Cu) is used to make machine bearings because it tends to reduce friction.



Courtesy of the Ford Motor Car Co. of Canada

FIG. 243—REPLACEABLE TYPE BABBIT BEARINGS SUPPORT THE MAIN CRANK-SHAFT OF AN AUTOMOBILE ENGINE

BISMUTH (Bi)

Bismuth is found in the free state in nature. It also occurs as the trioxide, Bi_2O_3, the trisulphide, Bi_2S_3, and as bismuth telluride, Bi_2Te_3. Most of the world's bismuth comes from Bolivia and Canada.

Bismuth is a lustrous, brittle, crystalline metal. It has a low melting point and, like antimony, expands on changing from the liquid to the solid state.

The chief use of bismuth is in the production of low-melting point alloys, such as Wood's metal and Rose's metal. These alloys have some important applications, being used in automatic sprinklers, electric fuses, and safety plugs for the prevention of boiler explosions. *Wood's metal* is an alloy containing bismuth, lead, tin and cadmium. The melting point of this alloy is 66° C., which is a lower temperature than the melting point of any of the components of the alloy. *Rose's metal* is an alloy made up of lead and tin. This alloy melts at 95° C. An important property of both these alloys is that they expand upon cooling, and this fact is made use of in many of the applications of alloys of this kind.

Certain compounds of bismuth are used in medicine. Bismuth subcarbonate ($Bi_2O_3 . CO_3 . H_2O$) is given to a person before an X-ray photograph is taken of their stomach. This compound is also used to neutralize excess acidity in the stomach.

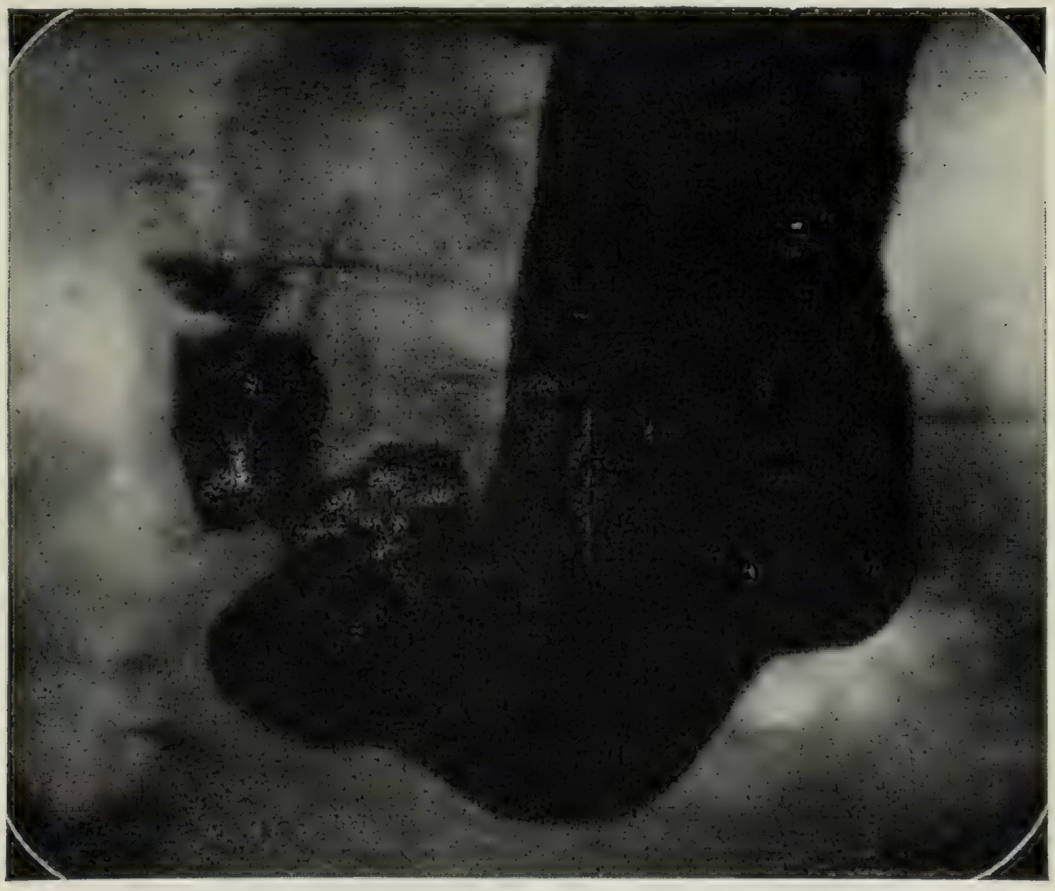


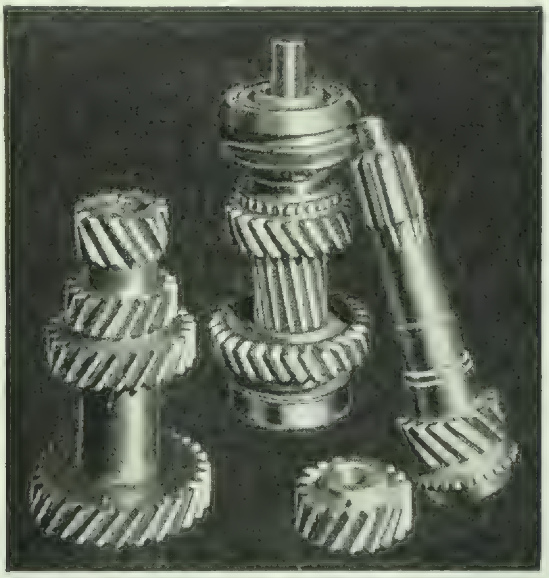
FIG. 244—AN X-RAY PHOTOGRAPH OF THE STOMACH. BISMUTH SUBCARBONATE IS GIVEN BEFORE THE PHOTOGRAPH IS TAKEN

CHROMIUM, MOLYBDENUM AND TUNGSTEN

(Some Group VI Metals)

CHROMIUM (Cr)

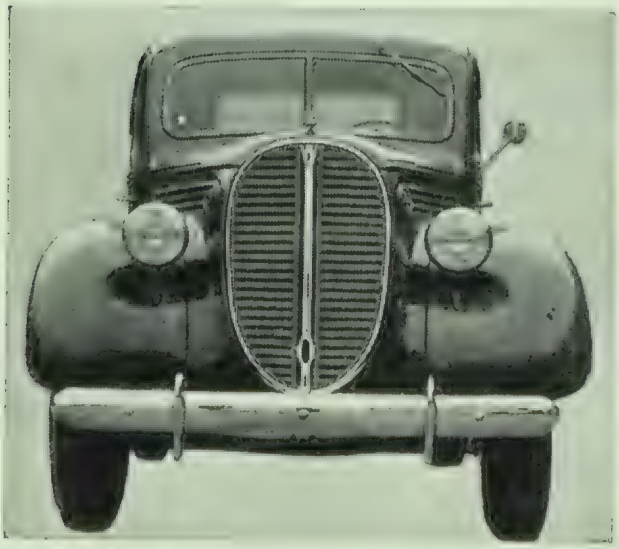
The chief ore of chromium is chromite, $Cr_2O_3.FeO$. This mineral is obtained chiefly from Turkey, Southern Rhodesia, South Africa and Cuba. It is prepared from its ore by the thermit process (see page 355).



Courtesy of Ford Motor Car Co. of Canada, Ltd.

FIG. 245—TRANSMISSION GEARS

These are forged from chrome steel.



Courtesy of Ford Motor Car Co. of Canada

FIG. 246—CHROMIUM HAS BEEN ELECTROPLATED UPON THIS TRUCK BUMPER TO PROTECT IT FROM CORROSION AND TO IMPROVE ITS APPEARANCE

Chromium is a bluish-white metal. It has a high metallic lustre, and will take a brilliant polish. Chromium is a very hard substance and its resistance to corrosion makes it an excellent material for use on automobiles. Its soluble compounds are extremely poisonous.

Chromium is a component of many important alloys which are used in anti-friction bearings, gears, cutlery and small tools. Chromite is also used in the production of refractory materials such as brick and cement, in the manufacture of chemicals, in electroplating, in dyeing, tanning and in certain pigments. Recently methods have been developed for electroplating with chromium. Objects such as automobile headlights and radiators, which are given a protective coating of chromium in this way, have a brilliantly lustrous surface which is extremely resistant to corrosion. *Stainless steel*, an alloy containing 11 to 15 per cent chromium, is used to a considerable extent for knife blades.

MOLYBDENUM (Mo)

Molybdenum is usually obtained from the mineral molybdenite (MoS_2), which is found in deposits in the United States and Canada. The pure metal is prepared by reduction with hydrogen or by the thermit process (see page 355). It usually comes to industry as ferro-molybdenum, carrying 60 to 65 per cent molybdenum, or as calcium molybdate, containing 35 to 45 per cent molybdenum. It is rather interesting to know that when this metal is alloyed with iron in amounts of less than one per cent, it gives to the alloy greater hardness, toughness and tensile strength.

TUNGSTEN (W)

Tungsten is one of the heavier metallic elements. Its outstanding property is the fact that it has a high melting point, 3380° C. The chief use of this metal is in the production of certain alloy steels, such as the permanent steel magnets used in magnetos. Tungsten tool steel will keep a cutting edge at very high temperatures (red-hot). Due to its high melting point, the most important use of tungsten is to make filaments in incandescent lamps, X-ray and radio tubes.

MANGANESE (Mn)
(A Group VII Metal)

Manganese is found in nature as *pyrolusite*, MnO_2, which is its chief ore. The Soviet Union is the largest producer of this metal, which is so important in the steel industry. It is also mined in Brazil, India and South Africa. Manganese can be prepared in the free state by the thermit process (see page 355). However, it is generally used in industry alloyed with iron. These alloys are prepared by reduction of the manganese ore (MnO_2) with carbon in the blast furnace.

Manganese is a hard, brittle, steel-like metal. It becomes tarnished on exposure to moist air because, like iron, it combines readily with the oxygen of the air. In its chemical properties this metal is similar to iron. Compounds of manganese are known in which the valence of the metal varies from two to seven.

The chief use of manganese is in the production of alloys, especially those of iron. *Spiegeleisen* is an important manganese-iron alloy. It contains variable amounts of manganese up to as much as 20 per cent, along with definite proportions of carbon. It is used to remove oxygen in the manufacture of steel, and as a way of adding carbon to steel in the Bessemer process. Ferromanganese is an alloy with a manganese content of almost 80 per cent. *Steels containing manganese* are very hard, and so are used in making *steel rails*, the *jaws of rock crushers*, *safes*, and *heavy machinery*.

COBALT, NICKEL AND PLATINUM

(Some Important Group VIII Metals)

COBALT (Co) and NICKEL (Ni)

1. Occurrence

Cobalt and nickel are two metals which play an important role in modern civilization. They are usually found together in ores which contain iron, silver and copper, in combination with arsenic and sulphur. The world's chief deposits of cobalt are located at Cobalt, Ontario, and in the Belgian Congo, while the chief mines of nickel are at Sudbury, Ontario, where over 85 per cent of the world's supply of nickel is mined. The mines at Cobalt are also rich in silver.

2. Properties

Both these metals are silvery in appearance and take a high polish. They are slightly heavier than iron and melt at a lower temperature. Unlike iron, these metals do not rust. Both cobalt and nickel are magnetic.

Cobalt, like iron, forms two classes of compounds, with valences two and three. The *cobaltous* salts are more important than the *cobaltic*. Nickel shows a valence of two or four. The *nickelous* salts, such as $Ni(NO_3)_2$, are, as a rule, green in colour. There are no salts of nickel in which this element has a valence of four. When carbon monoxide comes in contact with finely powdered nickel, at room temperatures, the compound *nickel carbonyl*, $Ni(CO)_4$, is produced. The *Mond process* for the separation of nickel from other metals depends upon the production of this compound, which can be distilled off as a vapour and is decomposed at 150°-180° C. to give free nickel and carbon monoxide.

3. Uses

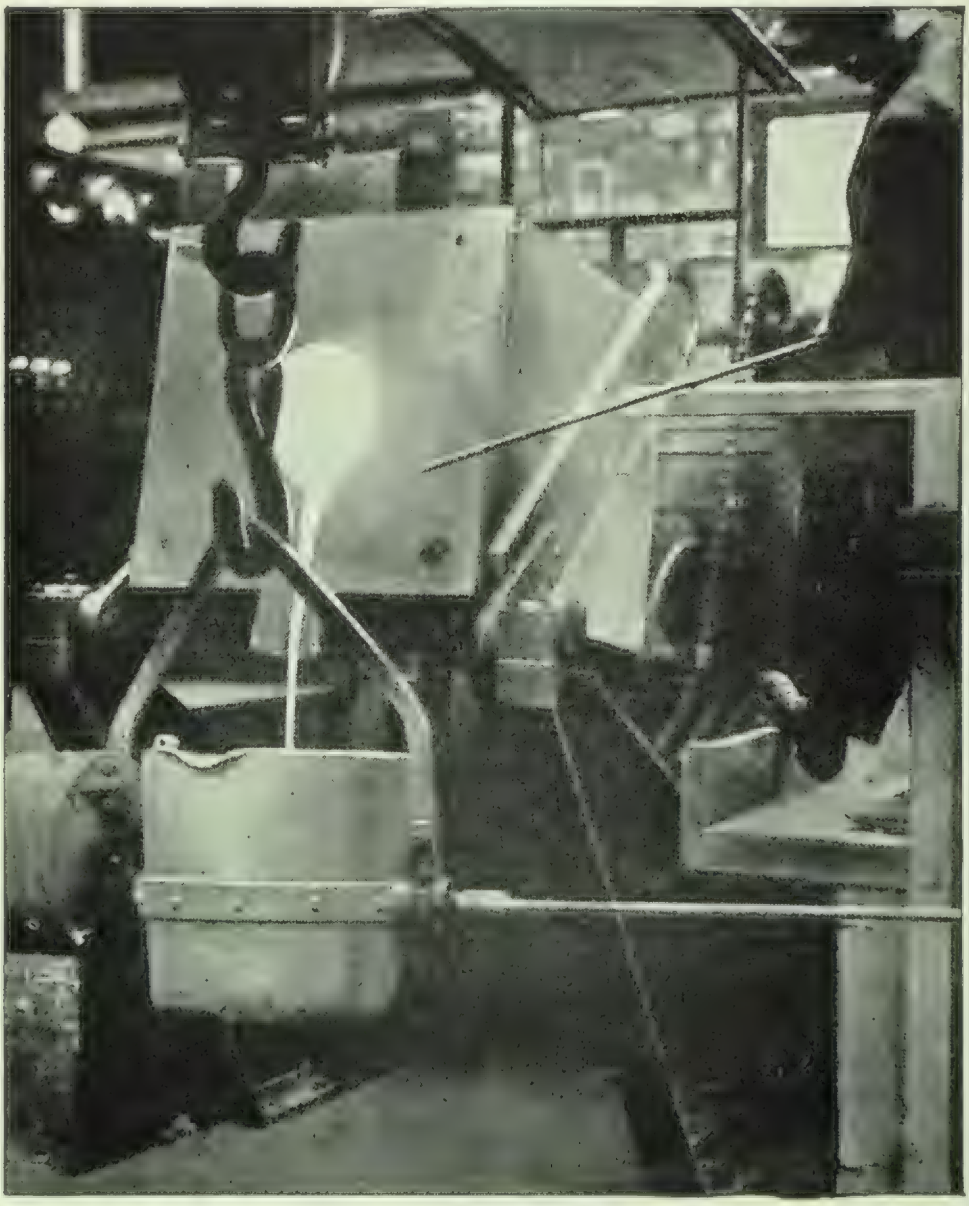
The chief uses of both nickel and cobalt are as alloy metals. When alloyed with iron, copper, chromium, silver, or with combinations of these, they give alloys of a very wide range of properties and uses.

Nickel steel is very hard and tough. It is used for structural purposes and to make armour plate. Nickel-chromium steel is still harder and is used for railway switch-points and crossings. An alloy of nickel and iron known as *permalloy* made possible an increase in cable communication from 800 to 1,500 signals per minute.

Monel metal (68 per cent nickel, 27 per cent copper, 5 per cent iron or manganese) and other alloys of similar composition are tough, possess high tensile strength (almost as strong as steel), and do not corrode easily. This type of alloy is used where pleasing appearance and resistance to mild corrosion are required, as in the construction of restaurant fixtures, washing machines, and soda fountains. Rifle bullets have about the same composition as monel metal.

Other alloys of nickel are resistant to heat and electricity and are used in electric heaters and electrical instruments. *Nichrome* (trade name) is a good example of this type of nickel alloy. *Invar* (steel with 38 per cent nickel) is an alloy with a low coefficient of expansion. It is used in watches, length standards and measuring tapes.

Metallic cobalt has no direct uses, but its alloys, which are similar to those of nickel, are of growing importance. The chief alloys are similar to *stellite* (trade name), a cobalt-chromium alloy with small amounts of tungsten or molybdenum. These alloys are very hard and are used for high-speed cutting tools, especially for lathe tools. Cobalt also forms an alloy with aluminum which is 85 per cent stronger and 100 per cent harder than aluminum. Alloys of cobalt are often employed in making permanent magnets. *Alnico*, an alloy of aluminum, nickel and cobalt, has remarkable magnetic properties.



Courtesy of Messrs. Hadfields Ltd., Sheffield

FIG. 247—POURING A CAST OF SPECIAL NICKEL-CHROMIUM HEAT RESISTING STEEL FROM A HIGH-FREQUENCY ELECTRIC FURNACE

PLATINUM (Pt)

Platinum is present as an impurity in the nickel ores at Sudbury. In spite of the fact that the quantity present is extremely small, the total amount recovered in the refining of nickel is so great that Canada leads the world in the production of this precious metal.

Platinum is a very heavy, silvery metal with a high melting point (1755° C.). It is unchanged by exposure to the air, acids, and most chemical reagents. However, it does react with chlorine, and so platinum dissolves in aqua regia.

The chief use of platinum is for *jewelry*, about half of the metal produced being used for that purpose. Due to its chemical inertness and high melting point, platinum is used as contact points in electrical apparatus, and for the making of *crucibles*, *evaporating dishes*, *wires* and similar pieces of apparatus for use in chemical laboratories. In the spongy or colloidal form (platinum black), platinum is used as a *catalyst* in the industrial production of many chemicals, such as sulphuric acid (contact process) and nitric acid (Ostwald process).

EXERCISES

1. (a) Write a note on the production of magnesium from Canadian dolomite.
   (b) Write a note on the uses of magnesium.
2. (a) What is the chief ore of zinc?
   (b) Write equations to show how free zinc is obtained from its ore.
   (c) Is zinc an amphoteric element? Illustrate your answer with equations.
   (d) Tabulate five uses of zinc.
3. Write a short note on cadmium.
4. (a) What is cinnabar?
   (b) Tabulate five uses of mercury.
5. Write a short note on indium.
6. (a) What element does titanium resemble?
   (b) Discuss the industrial importance of titanium.
7. (a) What is the chief ore of tin?
   (b) What is tin plate and how is it made?
   (c) Name three alloys containing tin.
   (d) Write the formulas for the following: stannous chloride, stannic chloride, stannous oxide, stannic oxide.
8. (a) What is the chief ore of lead?
   (b) Write a note on the metallurgy of lead.
   (c) Tabulate five properties of lead.
   (d) Tabulate five uses of lead.
   (e) What are the chief components of a paint?

9. (a) What is the chief ore of arsenic?
   (b) Write the equations for the following:
      (1) The heating of arsenopyrite.
      (2) The burning of arsenic in air.
      (3) The action of chlorine on arsenic.
      (4) The heating of zinc with arsenic.
   (c) What is the chief use of arsenic compounds?

10. (a) What is stibnite?
    (b) What is type metal?
    (c) What is Babbit-metal and what is it used for?

11. Discuss bismuth under the headings: (a) occurrence; properties; (c) uses.

12. Discuss the importance of chromium, molybdenum and tungsten in industry.

13. (a) What is the chief ore of manganese?
    (b) Write a note on manganese alloys.

14. Discuss cobalt and nickel under the headings: (a) occurrence; (b) properties; (c) uses.

15. (a) How is platinum obtained in Canada?
    (b) Tabulate five properties of this metal.
    (c) Tabulate five uses of platinum.

CHAPTER LIX

ATOMIC ENERGY

1. Isotopes

Early in the nineteenth century, John Dalton, an English school master, proposed his famous atomic theory. This stated that all the chemical elements were made up of very small, indestructible particles known as atoms. From the atoms of one or more of the elements all the different chemical compounds which exist in nature are built up. Dalton explained chemical reactions by means of atoms, and his ideas proved to be of great assistance in the explanation of the chemical behaviour of matter. One of Dalton's assumptions was that all atoms of a given element have the same atomic weight. In recent times it has been shown by two outstanding scientists, J. J. Thomson and F. W. Aston, that this postulate of Dalton's theory is not correct. They discovered that many elements have atoms of different weights. Fig. 248, shows the two different atoms of lithium. All lithium atoms have a charge on the nucleus of *three positive*, that is, they all have three protons in the nucleus. Also, every lithium atom has *one* electron in the outermost orbit. However, there are two varieties of lithium atoms. One type has an *atomic weight of six* and contains three protons and three neutrons in the nucleus. On the other hand, the other type has an *atomic weight of seven*, having three protons and four neutrons

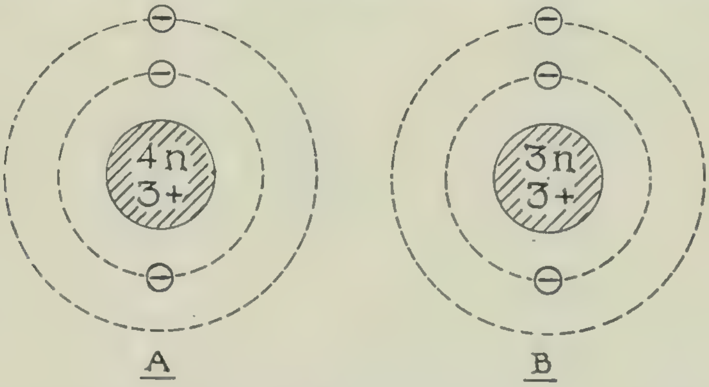


FIG. 248—DIAGRAMS OF THE ISOTOPES OF LITHIUM. A REPRESENTS THAT TYPE OF LITHIUM ATOM WHICH HAS AN ATOMIC WEIGHT OF SEVEN. B REPRESENTS THAT VARIETY OF LITHIUM ATOM WHICH HAS AN ATOMIC WEIGHT OF SIX

in the nucleus. Chemically, these two atoms are the same. Atoms of the same element, which have the same charge on the nucleus but different weights, are known as *isotopes* of that element. In the nucleus of all the isotopes of an element the *number of protons is the same.* It is the neutrons which vary in number, giving atoms of different weights.

Some isotopes are given in Table 32. The element chlorine, for example, as it is found in nature consists of a mixture of two isotopes of atomic weights, 35 and 37. Every sample of chlorine found in nature contains 76 per cent of the 35 isotopes and 24 per cent of the 37 variety. The atomic weight of this element determined by the usual atomic weight method is 35.457. This value represents the average atomic weights of the two isotopes.

TABLE 32—SOME ISOTOPES

Element	Atomic Number	Atomic Weight	Weight of Isotopes in Order of Abundance
Hydrogen	1	1.008	1, 2, 3
Lithium	3	6.94	7, 6
Oxygen	8	16.000	16, 18, 17
Neon	10	20.183	20, 22, 21
Magnesium	12	24.32	24, 25, 26
Chlorine	17	35.457	35, 37
Argon	18	39.944	40, 36, 38
Potassium	19	39.096	39, 41, 40
Zinc	30	65.38	64, 66, 68, 67, 70
Uranium	92	238.07	238, 235, 234

2. Radioactivity

A fundamental idea of Dalton's atomic theory was that the atoms of any one element could in no way be changed or converted into those of another element. The chief break with this theory took place towards the end of the nineteenth century when certain important discoveries were made in physics.

The first discovery came in 1895 when *Roentgen* discovered a new kind of radiation which could pass through glass and even opaque materials like flesh. The radiation affected a photographic plate in much the same way as light. These were *X-rays*, which are used by medical men to take pictures of the bones in the body. The X-ray has also found its place in industry. It is now possible to discover defects in various metals by the use of the X-ray. This is of great importance when metal is used in the construction of some object which will be subjected to enormous pressure and strain. The discovery of X-ray started scientists searching for new kinds of radiation.

It had been known for some time that compounds of the rare element uranium can be observed to glow slightly in a very dark room. In 1896, the French physicist, *Becquerel*, discovered that salts of uranium would affect a photographic plate, protected by black paper, just as X-rays did. He also found that when a charged electroscope is brought near any uranium compound the electroscope loses its charge. This proves that the air around the uranium compounds is an electrical conductor, which, of course, ordinary air is not. This property of uranium compounds was called *radioactivity*.

Pierre and *Madame Curie*, friends of Becquerel, made a thorough study of this phenomena of radioactivity. As a result of their researches they discovered, in 1898, a new element, *radium*. In a short time other elements, similar in properties to radium, were discovered and this group of elements is known as the radioactive elements. They give off radiations or particles of matter and in time, it may be thousands of years, they tend to reduce their atomic weight. That is, their atomic structure becomes simpler and they change into an inert element of lower atomic weight and number. For example, half of any given amount of radium, which has an atomic weight of 226, changes to radon (atomic weight 222) in about 1600 years. This period is known as the *half-life* of radium.

Because of the extremely strong powers of penetration possessed by the rays given off by radium, it has found many uses in science and industry. Outstanding is the development of its use in the treatment of some types of cancer and of numerous skin diseases. In industry radium is used in the production of a luminous paint, familiarly seen on the faces of clocks and watches.

Canada is fortunate in having large deposits of the mineral *pitchblende*, from which radium is obtained. These deposits are in the region of Great Bear Lake near the Arctic Circle. It is interesting to know that it takes about three tons of pitchblende, sometimes called uranium oxide, to produce one gram of radium. This process of securing radium from pitchblende is carried on in a refinery at Port Hope, Ontario.

It is from some of these unstable and radioactive elements that man has drawn atomic power. At the present time nature's heaviest atom, uranium, is the basic source of atomic energy.

3. Atomic Energy

There are two types of energy in the atom, *electron* and *nuclear*. It is known that the electrons in an atom move around the nucleus in orbits at very high speeds. The energy possessed by these tiny moving particles is, however, relatively small. The nucleus of the atom is made up of protons and neutrons bound together very firmly. This binding energy, known as nuclear energy, resists the separation of protons and neutrons, and it is very great. The nucleus of a helium atom contains two protons bound to two neutrons, and scientists have calculated that the nuclear energy of one pound of helium is equivalent to electrical energy sufficient to operate a 100-watt light bulb for 13,000,000 years.

Release of atomic energy rests upon three fundamental principles. These are:

(1) Matter can neither be created nor destroyed but only altered in form. (Law of Conservation of Matter).

(2) Energy can neither be created nor destroyed. (Law of Conservation of Energy).

(3) Einstein's principle of relativity, which is that mass and energy are really alternate forms of the same thing. This famous principle was first pointed out in 1905 and Einstein expressed his principle by means of the following equation:

$$E = mc^2$$

In this equation the E represents the amount of energy equivalent to any given mass m, and c is the velocity of light (186,300 miles per second). For example, if one kilogram (1000 grams) of a substance, which is about 2.2 pounds, could be changed into energy, it would give 25 billion kilowatt hours of energy. This would be equivalent to all the electrical power generated in the United States in the year 1939 for about two months.

When the atomic bombs were dropped on Japan, it was announced that each bomb was equivalent to 20,000 tons of T.N.T. However, the energy in the atomic bomb is not as great as for the figures obtained from Einstein's equation. This is because the atoms in the bomb are only split into a few fragments with the release of only a fraction of the energy which could be secured if the atom were completely disintegrated into neutrons and protons.

4. Atomic Fission

There is little evidence to show that element number 93 exists in nature. Scientists were interested in the possibility of building up artificially such an element by bombarding uranium with protons and neutrons. In 1939 definite results were obtained by two German scientists, Otto Hahn and F. Strassmann. They found that when neutrons bombarded samples of uranium, the uranium nucleus captured the neutrons. Then, unlike any other radioactive substance, the nucleus broke into two or more *large* pieces, each the size of a moderately heavy atom.

Immediately afterwards Lise Meitner and Otto Frisch pointed out that this discovery could only mean that, when uranium was bombarded by neutrons, a reaction took place in the nucleus of the uranium atom of a kind entirely different from any so far studied. They also believed that the uranium nucleus was split into two parts of approximately equal mass. These scientists called this phenomenon "atomic fission." They found that atomic fission only took place when *slow-moving* neutrons bombarded the isotope of uranium with an atomic weight of 235. This isotope, of course, has the same atomic number, namely 92, as ordinary uranium, and it can be represented as ${}_{92}U^{235}$. When a neutron hits the nucleus of the atom of this isotope, another isotope of uranium ${}_{92}U^{236}$ is formed.

$${}_{92}\mathbf{U}^{235} + \text{a neutron} \longrightarrow {}_{92}\mathbf{U}^{236}$$

${}_{92}U^{236}$ is not stable and at once breaks up, giving off several neutrons and forming two approximately equal masses which become the nuclei of two atoms, the sum of whose atomic number is 92. The liberated neutrons attack the other U-235 atoms. This causes a fresh fission, accompanied by the emission of more neutrons. A "chain reaction" thus occurs, releasing, in any pure sample of U-235, a tremendous amount of energy in a fraction of a second.

The question arises as to the source of neutrons. They are obtained in two ways: (a) from the atomic reactions inside the U-235 nucleus; (b) from cosmic rays, which continuously bombard the earth from outer space.

Another question is how to keep the U-235 from exploding until you want it to do so. In a small amount of U-235 the number of neutrons available for atom splitting is not large enough to start the chain reaction and resulting explosion. It is only when the size of the sample is such that the production of free neutrons by fission is greater than the loss of neutrons by escape, that we get a chain reaction. The size at which the fission reaction becomes self-sustaining is known as the *critical size.*

Uranium is a rare element and it only contains a small fraction (0.7 per cent) of U-235. It was a tremendous engineering feat to remove this small amount of U-235 from the ordinary variety of uranium, U-238. The minute quantity of U-235 in ordinary uranium limits the use of this isotope as a source of energy for military and industrial purposes, and so the discovery of plutonium, which can be made available in much larger quantities than U-235, was an important step forward in this field of research.

5. Plutonium

Experiments with moderate-velocity neutrons (3000 miles per second) showed that the neutrons did not split U-238 atoms, but combined with the U-238 nucleus to form a more complex atom, U-239. U-239 (atomic number 92) proved to be radioactive, emitting beta particles (electrons) and having a half-life of 23 minutes. Conversion of a neutron into a proton by the ejection of an electron converts U-239 into element 93, known as neptunium (Np). Neptunium, in turn, emits another beta particle (electron) and by doing so becomes element number 94, called plutonium (Pu). These changes can be summarized as follows:

$$
\begin{aligned}
{}_{92}\mathrm{U}^{238} + 1\ \text{neutron} &\longrightarrow {}_{92}\mathrm{U}^{239} \\
{}_{92}\mathrm{U}^{239} &\longrightarrow {}_{93}\mathrm{Np}^{239} + 1\ \text{electron} \\
{}_{93}\mathrm{Np}^{239} &\longrightarrow {}_{94}\mathrm{Pu}^{239} + 1\ \text{electron}
\end{aligned}
$$

The question arises as to why plutonium is not found in nature. The answer to this question is that neutrons escaping from the U-235 atoms travel so fast that they escape without doing any work. This can be prevented in two ways, first by increasing the quantity of U-235, and secondly by slowing down the neutrons by passing them through heavy water (molecular weight 20) or graphite. The substance used for slowing down the neutrons is called a "moderator." Graphite is generally used in the United States, while "heavy water" is being used in Canada.

The importance of plutonium lies in the fact that it undergoes chain fission when bombarded by neutrons. As already indicated, plutonium, Pu, is produced by allowing the neutrons emitted by U-235, as it undergoes fission, to strike against the atoms of U-238. Thus, U-238 can be used as the raw material and U-235 as the energy source, mixed in the same proportion as in natural uranium metal.

Plutonium is produced in a "pile" consisting of blocks of graphite interspersed with blocks of uranium metal. The moderator slows down the neutrons so that additional fission of U-235 maintains the reaction, and the U-238 nuclei capture the moderately moving neutrons. A "pile" in operation gives off considerable energy. Such piles may be the chief source of future atomic energy for commercial heat and power.

Uranium is found in nature in the following ores: pitchblende, carnotite, and uranite. These ores are found chiefly in the Great Bear Lake region in Canada and in Katanga Territory in the Belgian Congo.

Scientists have observed fission in other naturally occurring elements besides uranium. Thorium (atomic number 90) and protoactinium (atomic number 91) might be used as sources of atomic energy.

Canadian scientists played an important part in the research work leading up to the production of the atomic bomb. The Canadian government has established a large research centre at Chalk River, a few miles west of Ottawa, where radioactive materials will be produced in quantity for use in medical research. Other experiments will probably be conducted in an attempt to use atomic energy for industrial uses.

EXERCISES

1. (a) What are isotopes?
   (b) Make diagrams for the isotopes of lithium.
   (c) What are the isotopes of uranium?
2. (a) What did Roentgen discover?
   (b) What did Becquerel discover concerning salts of uranium?
3. Write a note on radium.
4. (a) What are the chief types of atomic energy?
   (b) What are the fundamental principles upon which the release of atomic energy rests?
5. (a) What is meant by atomic fission?
   (b) What is a chain reaction?
   (c) What is meant by the term critical size?
6. (a) How is plutonium produced?
   (b) Why is plutonium better than U-235?
   (c) What is meant by the term "pile?"
7. (a) What are the chief ores of uranium?
   (b) What other elements might be used as sources of atomic energy?

APPENDIX I

RULES FOR SOLUBILITY

(In Water)

1. All *sodium*, *potassium* and *ammonium* compounds are *soluble*.
2. All *nitrates*, *chlorates*, and *acetates* are *soluble*.
3. All *chlorides* are *soluble*, except mercurous, silver and lead—(lead chloride is slightly soluble in cold water and soluble in hot water).
4. All *sulphates* are *soluble*, except those of lead, barium, and calcium. Calcium sulphate is slightly soluble. Silver and mercurous sulphates are moderately soluble.
5. All normal *carbonates*, *phosphates* and *silicates* are *insoluble* except those of sodium, potassium and ammonium.
6. All *oxides* and *hydroxides* are *insoluble* except those of sodium, potassium, and ammonium. Barium hydroxide is moderately soluble and calcium hydroxide is slightly soluble.

APPENDIX II

APPROXIMATE SOLUBILITIES OF SOME COMMON SALTS

(Numbers refer to grams of anhydrons solute in 100 g. of water at 20° C. unless otherwise noted).

Ammonium chloride	37.0
Ammonium nitrate	192.0
Ammonium sulphate	75.0
Barium chloride	36.0
Barium nitrate	9.1
Barium sulphate	2.5×10^{-4}
Calcium carbonate	1.5×10^{-3}
Calcium chloride ($CaCl_2.6H_2O$)	75.0
Calcium nitrate	102.0 (at 0° C.)
Calcium sulphate	0.2
Copper sulphate	21.0
Lead chloride	1.0
Lead nitrate	57.0
Magnesium chloride ($MgCl_2.6H_2O$)	55.0
Magnesium nitrate ($MgNO_3.6H_2O$)	42.5
Potassium carbonate	112.0
Potassium chloride	34.0
Potassium nitrate	32.0
Potassium sulphate	11.1
Silver chloride	1.5×10^{-4}
Silver nitrate	122.0
Sodium bicarbonate	9.5
Sodium carbonate ($Na_2CO_3.10H_2O$)	21.5
Sodium chloride	36.0
Sodium nitrate	88.0
Sodium sulphate ($Na_2SO_4.10H_2O$)	19.5
Zinc sulphate	86.5

APPENDIX III

REVIEW EXERCISES

1. (*a*) State the Kinetic Molecular Hypothesis.
   (*b*) State Charles' law and Boyle's law.
   (*c*) Show clearly how the Kinetic Molecular Hypothesis accounts for either *one* of these laws.

2. (*a*) Name the components of the atmosphere.
   (*b*) State the function of each of the more important components.
   (*c*) What proof is there that air is not a compound?

3. (*a*) State the Ionic Hypothesis.
   (*b*) By means of ionic equations show what is meant by an *acid*, a *base*, a *salt*, *neutralization*.
   (*c*) What is the difference between an atom and an ion?

4. (*a*) What is an acid anhydride? Give one example.
   (*b*) What type of elements form acid anhydrides?
   (*c*) What is a basic anhydride? Give one example.
   (*d*) What type of elements form basic anhydrides?

5. (*a*) What is meant by each of the following terms applied to solutions: unsaturated, supersaturated, saturated.
   (*b*) How may each of the first two types be converted into the third?

6. In the Haber Process for the fixation of nitrogen
   ($N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3 +$ heat), is it desirable to use
   (*a*) high or low pressure?
   (*b*) high or low temperature?
   (*c*) a catalyst?

   Give reasons for your answers.

7. (*a*) Give two methods for the preparation of sulphur dioxide.
   (*b*) Tabulate the physical and chemical properties of sulphur dioxide.
   (*c*) State two important uses of sulphur dioxide.

8. (*a*) Give one method for the preparation of nitric acid.
   (*b*) Tabulate the physical and chemical properties of nitric acid.
   (*c*) State one important use of nitric acid.
   (*d*) How would you test a solution for the presence of nitrate ion?

9. (*a*) Give one method for the preparation of hydrogen chloride.
   (*b*) Tabulate the physical and chemical properties of hydrogen chloride.
   (*c*) State one important use of hydrogen chloride.
   (*d*) How would you test a solution for the presence of chloride ion?

10. (*a*) What are hydrocarbons?
    (*b*) Give the name, occurrence, properties and an important use of of any *one* example.

11. Write briefly on the sources, industrial preparation, properties and uses of acetic acid.

12. (*a*) State Arrhenius' Theory of Ionization.
    (*b*) In terms of this theory, explain the electrolysis of water.
    (*c*) Also, in terms of this theory, account for the difference between a "strong" acid and a "weak" acid.

13. (*a*) State the Law of Conservation of Mass.
    (*b*) Show how the method of determining the per cent of water in a hydrate assumes the truth of the Law of Conservation of Mass.
    (*c*) State the Law of Conservation of Energy.

14. Name four types of chemical change and give one example of each.

15. (*a*) What is meant by the "cracking" of petroleum?
    (*b*) What products are obtained from the distillation and cracking of petroleum?

16. (*a*) Outline the preparation of ethanol (ethyl alcohol).
    (*b*) Tabulate the properties of ethanol.
    (*c*) Name some of the uses of ethanol.

17. (*a*) Tabulate the properties of ammonia and of ammonium hydroxide.
    (*b*) Distinguish between the ammonium radical and ammonia.
    (*c*) Describe a chemical test for ammonium salts.

18. (*a*) Name four processes that may be employed in the purification of water.
    (*b*) State the purpose for which each is used.

19. (*a*) Give two methods for the preparation of carbon dioxide.
    (*b*) Tabulate the properties of carbon dioxide and of carbonic acid.
    (*c*) How would you test a solution for the presence of carbonate ion?

20. (*a*) Describe briefly the principal steps in the contact process for the manufacture of sulphuric acid.
    (*b*) Tabulate the properties of sulphuric acid and distinguish carefully between those of the concentrated and those of the dilute acid.

21. (*a*) Describe two methods for the preparation of chlorine.
    (*b*) Tabulate the physical and chemical properties of chlorine.
    (*c*) State two uses of chlorine.

22. (*a*) How does iron occur in nature?
    (*b*) What is "pig iron" and how is it produced?

23. (*a*) In terms of Arrhenius' Theory of Ionization, define an acid, a base, and a salt.
    (*b*) Give an example of electroplating and explain the process in terms of the Theory of Ionization.

24. (*a*) What is meant by a "reversible reaction"?
    (*b*) Give the balanced equation for one example of such a reaction.
    (*c*) Give the balanced equation for one example of a reaction that goes practically to completion.

25. (*a*) What is meant by each of the following terms applied to solutions: unsaturated, saturated, supersaturated?
    (*b*) What effect has an un-ionized solute on the freezing point and on the boiling point of water?

26. (*a*) What is meant by the "destructive distillation" of soft coal?
    (*b*) Name the principal products obtained from this process.

27. (*a*) What is a "hydrocarbon"?
    (*b*) Name the principal series of hydrocarbons and give the general formula of each series.

28. (*a*) Describe two methods for the preparation of oxygen.
    (*b*) Tabulate the physical and chemical properties of oxygen.
    (*c*) Describe a test for oxygen.

29. (*a*) Describe two methods for the preparation of nitric acid.
    (*b*) Tabulate the physical and chemical properties of nitric acid.
    (*c*) How would you test a solution for the presence of nitrate ion?

30. (*a*) How may hydrogen sulphide be prepared?
    (*b*) Give the balanced equation for the reaction.
    (*c*) State the properties of hydrogen sulphide and those of its solution in water.
    (*d*) How would you test a solution for the presence of sulphide ion?

31. (*a*) How does sulphur occur in nature?
    (*b*) Outline a process by which it is mined.
    (*c*) Tabulate the physical and chemical properties of sulphur.

32. (*a*) Outline the method by which pure aluminum is produced.
    (*b*) State the physical properties of aluminum.
    (*c*) Give the name, properties and uses of one important alloy of aluminum.

33. (*a*) State the assumptions made in Dalton's Atomic Theory.
    (*b*) What is meant by "atomic weight"?

34. (*a*) State the Law of Conservation of Energy.
    (*b*) Give two reactions as examples of different forms of energy associated with chemical change.

35. (*a*) What is meant by the Electromotive (or displacement) Series?
    (*b*) On what basis is it arranged?

36. (*a*) Compare the common properties of acids with those of bases.
    (*b*) Explain what is meant by neutralization.

37. (*a*) What is the difference between a mixture and a compound?
    (*b*) Give two reasons for the conclusion that air is a mixture and not a compound.

38. (*a*) Outline a method for the preparation of methanol (methyl alcohol).
    (*b*) State the properties of methanol.
    (*c*) Give two uses of methanol.

39. (*a*) Make a concise list of the physical and chemical properties of sodium.
    (*b*) Describe an electrolytic method for the preparation of sodium hydroxide.

40. (*a*) Write briefly on the occurrence of carbon in nature.
    (*b*) Compare the properties and uses of the two crystalline forms of carbon.

41. (*a*) Outline two methods for the preparation of ammonia.
    (*b*) Tabulate the physical and chemical properties of ammonia.

42. (*a*) Give the balanced equation for the preparation of hydrogen chloride.
    (*b*) Tabulate the physical and chemical properties of hydrogen chloride and state how its water solution differs from the pure compound.
    (*c*) How would you test a solution for the presence of chloride ion?

43. Name four types of chemical change and, in the form of balanced equations, give one example of each.

44. (*a*) What is "valence"?
    (*b*) From the electronic standpoint, show why each of the following reactions is one of oxidation and reduction:

$$\mathrm{Zn} + \mathrm{S} \longrightarrow \mathrm{ZnS}$$

$$2\ \mathrm{FeCl_3} + \mathrm{H_2} \longrightarrow 2\ \mathrm{FeCl_2} + 2\ \mathrm{HCl}$$

45. (*a*) How is ethanol (ethyl alcohol) prepared?
    (*b*) Make a list of the properties of ethanol.
    (*c*) State two uses of ethanol.

46. (*a*) Describe the preparation of cane sugar.
    (*b*) Give one source and one common use of glycerine (glycerol) and of ether.

47. (*a*) Give two methods for the preparation of hydrogen.
    (*b*) Tabulate the physical and chemical properties of hydrogen.
    (*c*) State two uses of hydrogen.

48. (*a*) Give two methods for the preparation of sulphur dioxide.
    (*b*) Tabulate the physical and chemical properties of sulphur dioxide.
    (*c*) State two uses of sulphur dioxide.

49. (*a*) Write the balanced equation for the reaction usually employed to prepare hydrogen sulphide.
    (*b*) Tabulate the physical and chemical properties of hydrogen sulphide.
    (*c*) Give an important property of its water solution.
    (*d*) Outline a test for the sulphide ion.

50. (*a*) Give two methods for the preparation of nitric acid.
    (*b*) Tabulate the physical and chemical properties of nitric acid.
    (*c*) Describe a test for the nitrate ion.

51. (*a*) Describe the process by which pig iron is obtained from iron ore.
    (*b*) What effect has the carbon content on the properties of iron?

52. (*a*) If a given weight of dry gas at a given temperature and pressure has its pressure doubled while its volume remains constant, what change must have taken place in its absolute temperature?
    (*b*) State the law involved in the above temperature change.
    (*c*) Show that the Kinetic Molecular Hypothesis offers a satisfactory explanation of Boyle's Law.

53. (a) Explain briefly the structure of the atom in terms of the Electron Theory. Illustrate your answer.
    (*b*) What is the difference between a hydrogen atom and a hydrogen ion?
    (*c*) Explain how the ammonium radical differs from the ammonia molecule.

54. (*a*) You are given in the laboratory three bottles of gas and are told that they contain one of the following: oxygen, carbon dioxide, or hydrogen sulphide. Test one bottle for oxygen, one for carbon dioxide and the remaining bottle for hydrogen sulphide.
    (*b*) Three unlabelled bottles contain dilute water solutions of hydrochloric acid, nitric acid, sulphuric acid, respectively. Devise tests to determine the label to be placed on each bottle.

55. What would be observed visually in the following experiments? Write chemical equations correctly balanced for the reactions involved:
    (*a*) Powdered antimony (Sb) is dusted into a jar of chlorine gas.
    (*b*) Metallic sodium is placed in water.
    (*c*) Concentrated nitric acid is dropped on red hot charcoal.
    (*d*) A strip of hot copper is held in the fumes of sulphur.

56. (*a*) What is a hydrocarbon? Give the graphic formula for methane.
    (*b*) What relationship exists between methyl alcohol and methane?
    (*c*) State a method of preparation and two uses of methyl alcohol.

57. (*a*) Glycerine is an important war commodity. What are two of its uses?
    (*b*) When dissolved in one litre of water which would cause the greater lowering of the freezing point—a gram molecular weight of acetic acid or a gram molecular weight of sugar? Why?
    (*c*) Name the source and one use of benzene and ether.

58. (*a*) What are the chief ores of aluminum?
    (*b*) Describe the method of preparing aluminum. Why is it manufactured where there is abundant electric power?
    (*c*) What properties of aluminum make it suitable for use in the manufacture of aircraft?

59. (*a*) Why is manganese dioxide used in the preparation of oxygen from potassium chlorate?
    (*b*) Why is manganese dioxide used in the preparation of chlorine from hydrochloric acid?
    (*c*) Name three factors which increase the speed of a chemical reaction.
    (*d*) Under what conditions will a chemical reaction go practically to completion?

60. (*a*) State two methods for the preparation of sulphur dioxide.
    (*b*) Write the equations for the chemical reactions involved.
    (*c*) Why is it that sulphur dioxide is a bleaching agent only in the presence of water?

61. Draw a diagram for the apparatus used for the preparation and collection of hydrogen, using zinc and dilute H_2SO_4, and contrast it with the apparatus used for the preparation and collection of chlorine from manganese dioxide and strong hydrochloric acid. Point out the difference and list the precautions to be taken in each case.

62. Write the equations for the following chemical reactions, and state the type of chemical reaction involved:
    (*a*) A solution of sodium hydroxide reacts with a solution of hydrochloric acid.
    (*b*) Ammonium hydroxide is heated.
    (*c*) Copper oxide is heated while hydrogen gas is passing over it.
    (*d*) Sulphur is burned in oxygen.

63. (*a*) State Arrhenius' Theory of Ionization.
    (*b*) By means of this hypothesis explain what is meant by an acid, base, salt, electrolyte.
    (*c*) How does a weak acid differ from a strong acid?
    (*d*) Write the ionic equation for the neutralization of sodium hydroxide by hydrochloric acid.

64. (*a*) State the assumptions made in Dalton's Atomic Theory.
    (*b*) Name two laws explained by this theory.
    (*c*) Does the modern electron theory of the atom make certain of Dalton's assumptions incorrect? If so, explain.

65. (*a*) In the laboratory you are given samples of three different white solids. You are told that each is soluble in water, and that one is a carbonate, one a sulphate, and one a chloride. Describe tests by which you could identify each.
    (*b*) State a simple test by which you could identify an ammonium salt.

66. What would be observed visually in the following experiments? Write chemical equations correctly balanced for the reactions involved:
    (*a*) Powdered sulphur and powdered iron are mixed in a mortar, placed in a test tube, and heated to kindling temperature.
    (*b*) Copper turnings are treated with hot concentrated sulphuric acid.
    (*c*) A mixture of copper oxide and carbon (charcoal) is placed in a test tube heated to a high temperature, and the gas evolved passed into lime water.
    (*d*) Hydrogen sulphide gas is passed into a solution of lead acetate.

67. (*a*) What is the meaning of *destructive distillation?*
    (*b*) What substances are produced during the destructive distillation of soft coal?
    (*c*) State the source and one use for each of the following: acetic acid, ethyl alcohol, ether.

68. (*a*) Why is hydrogen used to inflate balloons? What danger is there in its use?
    (*b*) What gas is formed in the ordinary fire extinguisher?
    (*c*) State two reasons why air is considered a mixture.
    (*d*) Carbon monoxide is a good fuel for gas stoves. Why is it dangerous to use?
    (*e*) Write the graphic formula for methane.
    (*f*) What chemical element is used to purify water, bleach cotton, and make poisonous war gases?

69. (*a*) Name two compounds of iron found in nature.
    (*b*) How is pig iron produced from the iron ore?
    (*c*) Pure iron is tough but soft; how can it be hardened to make steel?

70. (*a*) Describe the contact process for the production of sulphuric acid.
    (*b*) Write the equations for the chemical reactions involved.
    (*c*) State two important commercial uses for sulphuric acid.

71. (*a*) Explain valence according to the electron theory.
    (*b*) What is the difference between a normal salt and an acid salt? Write a formula for a normal and one for an acid salt of sulphuric acid.
    (*c*) State two general methods used to produce salts.

72. (*a*) How is ammonia produced in nature?
    (*b*) How did you produce and collect ammonia in the laboratory? Write the equation for the chemical reaction involved.
    (*c*) What effect, if any, has dry ammonia on dry red litmus paper?
    (*d*) How could you show that ammonia is soluble in water?

73. (*a*) What is an acid anhydride? Give one example.
    (*b*) What type of elements form acid anhydrides?
    (*c*) What is a basic anhydride? Give one example.
    (*d*) What type of elements form basic anhydrides?

APPENDIX IV

REVIEW PROBLEMS

1. Calculate the volume of dry hydrogen chloride (gas) produced under laboratory conditions of 20 degrees centigrade and pressure of 750 mm. of mercury, when 20 grams of sodium chloride are acted upon by an excess of concentrated sulphuric acid.
2. A certain mass of gas occupies a volume of 5 litres at a temperature of –23° C. and a pressure of 570 mm. of mercury. Calculate its volume at 227° C. and 760 mm. of mercury.
3. The formula of carbon tetrachloride is CCl_4.
   Calculate its percentage composition.
4. Calculate the weight of potassium chlorate that would be required to give 10 litres of dry oxygen measured at standard temperature and pressure.
5. A certain quantity of gas occupies a volume of 60 litres at a pressure of 760 mm. of mercury. What will be the volume of the gas when the pressure is 570 mm.?
6. Calculate the volume of dry nitrogen, measured at 25° C. and a pressure of 770 mm. of mercury, that would be obtained from the decomposition of 5 grams of ammonium nitrite (NH_4NO_2).
7. During the heating of a specimen of pure potassium chlorate the loss in weight of the potassium chlorate was 2 g. The oxygen liberated was collected at 18° C. and a pressure of 745 mm. of mercury. Calculate the volume of the oxygen. (Molecular weight of oxygen, 32)
8. Calculate the volume of hydrogen measured at 20° C. and 770 mm. of mercury that would be obtained if 10 g. zinc were allowed to react completely with excess dilute sulphuric acid.
9. A gaseous compound has the following composition: 96.2 per cent As, 3.8 per cent H. A volume of 1 litre of this gas measured at 0° C. and 760 mm. of mercury weighs 3.48 g. Find the formula of the compound.
10. If 1 litre of hydrogen, measured at a temperature of 30° C. and a pressure of 780 mm. of mercury, is to be obtained by allowing magnesium to react completely with excess hydrochloric acid, calculate the weight of magnesium required.
11. Calculate the volume of dry oxygen measured at a temperature of 20° C. and a pressure of 750 mm. mercury that would be obtained by heating 5 grams of potassium chlorate.

12. Calculate the volume of oxygen measured at 300° C. and 740 mm. of mercury that would react completely with 1 g. carbon to form carbon dioxide. What volume of carbon dioxide measured under the same conditions of temperature and pressure would be obtained?
13. A compound of carbon and hydrogen gives, on analysis, 92.3 per cent carbon and 7.7 per cent hydrogen by weight.
    (*a*) Find the simplest formula.
    (*b*) If the molecular weight is 26, what is the molecular formula?
14. If two grams of calcium carbide are treated with an excess of water, what volume of acetylene measured at standard temperature and pressure would be produced?
15. What weight of calcium carbonate can be obtained by the action of carbon dioxide on twenty grams of calcium hydroxide?
16. What volume of oxygen at 15° C. and 740 mm. pressure can be obtained from 327 grams of potassium chlorate?
17. The formula of borax is $Na_2B_4O_7 . 10H_2O$. Determine its percentage composition.
18. The formula for methane is CH_4. Find the weight in grams of 100 litres of methane at minus 20 degrees centigrade and 800 mm. of mercury.
19. Benzene has the formula C_6H_6. Calculate its percentage composition.
20. What weight of iron would be formed from the complete reduction of 1 ton (2000 lbs.) of iron ore, Fe_2O_3, by carbon monoxide?
21. Calculate the volume of hydrogen sulphide gas measured at 17°C, and 770 mm., that would be obtained if 20 grams of ferrous sulphide were allowed to react with an excess of dilute sulphuric acid.

APPENDIX V

COLOUR SCALE OF TEMPERATURE

Colour	*Temperature ° C.*
Dull Red	500-550
Dark Red	650-750
Bright Red	850-950
Yellow-Red	1050-1150
Dull White	1250-1350
Bright White	1450-1550

APPENDIX VI

REFERENCE BOOKS

Chemical Pioneers, (Haynes), D. Van Nostrand Company, N. Y.
Chemical Science, An Introduction to, (Hatcher), John Wiley & Sons, N. Y.
Chemistry at Work, (McPherson, Henderson, Fowler), Ginn & Co.
Chemistry in Agriculture, (Chamberlain), Chemical Foundation, N. Y.
Chemistry in Industry, Vols. I and II, (Howe), Chemical Foundation, N. Y.
Chemistry in Medicine, (Stieglitz), Chemical Foundation, N. Y.
College Chemistry, (Briscoe), Houghton Mifflin Company.
Creative Chemistry, (Slosson), The Century Company.
Crucibles, the Lives and Achievements of the Great Chemists, (Jaffe), Simon & Schuster, N. Y.
Elementary Chemistry, (Brownlee and Fuller), Allyn and Bacon.
Famous Chemists, The Men and Their Work, (Tilden), Geo. Routledge & Sons, Ltd., London.
General Chemistry, (Timm), McGraw-Hill Book Company.
General Chemistry, (Young and Porter), Prentice-Hall, Inc., N. Y.
General Chemistry, Introductory, (Brinkley), The Macmillan Co., N. Y.
General College Chemistry, (Richardson and Scarlett), Henry Holt and Company.
High School Chemistry Review, (Stannard), Oxford Book Company, N. Y.
Historical Introduction to Chemistry, (Lowry), The Macmillan Co.
History of Chemistry, A., (Moore), McGraw-Hill Book Company.
How to Make and Use a Small Chemical Laboratory, (Yates), Norman W. Henley Publishing Co., N. Y.
Industrial Chemistry, (Read), John Wiley & Sons, N. Y.
Industrial Chemistry, (Rogers), Van Nostrand Company.
Industrial Chemistry, (Riegel), Reinhold Publishing Corp., N. Y.
Inorganic Chemistry, (Jones), The Blakiston Company, Toronto.
In the Realm of Carbon, (Deming), John Wiley & Sons, N. Y.
Lecture Demonstrations in General Chemistry, (Arthur), McGraw-Hill Book Company.
Life of Pasteur, (Vallery-Radot), Doubleday, Doran & Company.
Madame Curie, (Eve Curie), Doubleday, Doran & Company.
Manual of Laboratory Glass-Blowing, (Wright), Chemical Publishing Company, 26 Court St., Brooklyn 2, N. Y.
Modern Inorganic Chemistry, (Mellor), Longmans, Green & Co., London.
New Practical Chemistry, (Black and Conant), The Macmillan Co.
Outline of First Year College Chemistry, (Lewis), Barnes & Noble, N. Y.
Out of the Test Tube, (Holmes), Emerson Books, 251 West 19th St., New York 11.
Questions and Answers in Chemistry, (Hess), College Entrance Book Company, N. Y.

Senior Chemistry, (Cornish), Copp Clark Company, Toronto.
Simple Chemical Experiments, (Morgan), D. Appleton-Century Co., N. Y.
Smith's Inorganic Chemistry, (Kendall), D. Appleton-Century Co., N. Y.
So You Want To Be a Chemist? (Coith), McGraw-Hill Book Company.
The Chemistry of Organic Compounds, (Conant), The MacMillan Co.
The Romance of Chemistry, (Foster), Century Company, N. Y.
This Chemical Age, (Haynes), Alfred A. Knopf, 501 Madison Avenue, N. Y.
Visualized Chemistry, (Lemkin), Oxford Book Company, N. Y.
Vitalized Chemistry, (Des Jardins), College Entrance Book Company, N. Y.

APPENDIX VII

*MOVING PICTURES

A. Sources of Moving Pictures.

(1) Associated Screen News,
1330 Sherbrooke St. West,
Montreal, P.Q.

(2) Department of Education,
Film Library,
Quebec, P.Q.

(3) Eastman Kodak Co.,
Teaching Films Division,
Toronto, Ont.

(4) Montreal Protestant Central School Board,
3460 McTavish St.,
Montreal 2, P.Q.

(5) National Film Board of Canada,
Ottawa, Ont.

(6) U. S. Department of the Interior,
Bureau of Mines,
4800 Forbes St.,
Pittsburg, Pa., U.S.A.

B. List of Moving Pictures.

All the films in this list are 16 mm. The name of the producer, if known, is placed in brackets after the title of the film and the source of the film is indicated by a number according to the list of sources given in Section A. For example, the film entitled "Distillation" was produced by the Shell Film Unit. It can be obtained from the Quebec Department of Education or from the Montreal Protestant Central School Board, and so this film is listed as follows: *Distillation* (Shell), sound, 9 mins., (2) or (4).

Abrasives (Carborundum Co.), silent, 2 reels, (6).
Air, Liquid, sound, 10 mins., (2).

Aluminum: Mine to Metal (Aluminum Co. of America), silent, 2 reels, (6).
Asbestos, The Story of (Johns-Manville Corp.), silent, 2 reels, (6).
British Guiana and its Bauxite (Aluminum Company of Canada, Montreal), sound, colour, (2).
Carbon-Oxygen Cycle, silent, (2).
Celite, The Story of the Diatom (Canadian Johns-Manville Co., Toronto), sound.
Coal, Anthracite, silent, (2) or (4).
Coal, sound, 800 ft., (4) or (2).
Copper (Phelps Dodge Corp.)
  —*Leaching and Concentration*, silent, 1 reel, (6).
  —*Refining*, silent, 1 reel, (6).
  —*Smelting*, silent, 1 reel, (6).
Copper, The Mining and Smelting of, silent, 1 reel, (1).
Chemistry and a Changing World (Erpi), sound, 10 mins., (4).
Chemistry of Combustion, silent, (2).
Chemical Effects of Electricity (Eastman), silent, 15 mins., (1) or (4).
Colloids (Erpi), sound, 10 mins., (2).
Crystals, sound, 7 mins., (2).
D.D.T., The Story of (Naugatuck Chemicals Ltd., Elmira, Ont.).
Distillation (Shell Film Unit), sound, 9 mins., (2) or (4).
Electrochemistry (Erpi), sound, 10 mins., (2).
Electrons, sound, (4).
Energy from Sunlight, silent, (4).
Explosives (Hercules Powder Co., Wilmington, Delaware), silent, 30 mins.
Fire Making (Eastman), silent, 15 mins., (2).
Gas Engine, Four Stroke, silent, (4).
Glass, The Story of Its Manufacture—Sand and Flame (General Motors Corp.), (2).
Glass, Safety (Ford Motor Co.), silent, 2 reels, (6).
Gold, silent, 1 reel, (1) or (4).
Gold, From Gold to Bullion (National Film Board), sound, (5).
Historical Introduction to the Study of Chemistry (Eastman), silent, 15 mins., (2).
Iron Ore to Pig Iron, silent, (1) or (4).
Lead, silent, 1 reel, (1) or (4).
Limestone and Marble (Eastman, silent, 15 mins., (2).
Match, Chemistry of a, silent, 10 mins., (2).
Molecular Theory of Matter (Erpi), sound, 10 mins., (2) or (4).
Nickel (The International Nickel Co. of Canada, Ltd., Toronto 1, Ont.)
  Nickel (U. S. Bureau of Mines), silent, 2 reels.
  Mining, Smelting and Refining of Copper—Nickel Ores, sound, 50 mins.
  Monel Metal, silent.
  The Story of Nickel, sound, 10 mins.
Nitrogen Cycle, silent, (2).
Oil, From the Earth (Shell), sound, 700 ft., (4).
Oil, Producing Crude, silent, 1 reel, (1).

Oil, Refining Crude, silent, 1 reel, (1).
Oxidation and Reduction (Erpi), sound, 10 mins., (2).
Oxyacetylene Torch, Story of—No Keener Blade (Canadian Liquid Air Co., Montreal), sound, colour, 30 mins.
Paper (Howard Smith Paper Co.), sound, colour.
Petroleum, sound, 2 reels, (4).
Pig Iron to Steel, silent, 1 reel, (1).
Pulp and Paper (International Paper Sales Co. Inc., Sun Life Bldg., Montreal), silent, 1400 ft.
Refrigeration, silent, 1 reel, (1) or (4).
Rubber, silent, 2 reels, 400 ft. (4).
R. for Rubber (National Film Board), sound, 8 mins., (5).
Salt, Common, silent, 1 reel, (4).
Silver, silent, 1 reel, (1).
Soap, silent, 1 reel, (1).
Steel, Story of, sound, (2).
Sugar Cane Industry, silent, (4).
Sulphur (Texas Gulf Sulphur Co.), silent, 2 reels, (6).
Water, Mysteries of, sound, 1 reel, (1) or (2).
Water, Properties of, sound, 10 mins., (2).
Water, Purifying, silent, 1 reel, (1) or (2).
Velocity of Chemical Reactions (Erpi), sound, 10 mins., (2).
Vision Fulfilled (Atlas Steels Ltd., Welland, Ont.), sound, colour, 50 mins.

*This list was prepared with the assistance of The Chemical Institute of Canada

ANSWERS TO PROBLEMS

Page 9
7: 34,000.

Page 13.
1: 2,500,000.
2: 299,991.30.
3: 3,900,000.
4: 2.016.
5: 4.80.

Page 45
5: Ca, 40%; C, 12%; O, 48%.
6: 9.26.
7: Si, 46.67%; O, 53.33%.
8: Na, 39.32%; Cl, 60.68%.
9: 0.80 g. H_2 and 6.4 g. O_2.
10: 7.41.
11: Ca, 54.05%; O, 43.24%; H, 2.71%
12: Al, 52.94%; O, 47.06%.
13: 249.6
14: 33.33.

Page 55
3: 3.66 g. KCl; 2.00 g. MnO_2.
11: 39.18.
12: 2552.08.
13: 50.
14: 2.76.

Page 71
11: 266.67.
12: 2.86.

Page 82
15: 72,000 g. H_2 and 1,034,400 g. of air.
16: 0.31.

Page 86
1: (1) 800 c.c.; (2) 1600 c.c.; (3) 152,000 c.c.; (4) 217.14 c.c.; (5) 152 c.c.
2: 12 c.c.
3: 584.21 c.c.
4: 2000.
5: 950 c.c.

Page 90
1: 600 c.c.
2: 300 c.c.
3: 327.
4: 177.
5: 500 c.c.

Page 94
1: 157.5 c.c.
2: 726.3 c.c.
3: 981.4 c.c.

Page 95
4: 294.2 c.c.
5: (a) 70.36 c.c. (b) 257.3 c.c.
6: 1125 c.c.
7: 2000 c.c.
8: 32 lbs.
9: 181.5 c.c.
10: 809.3 c.c.

Page 109
12: 88.86% O_2 and 11.14% H_2.

Page 114
2: 64.064.

Page 115
3: 35.69.
5: 39.52.
6: 65.56.
7: 5.89 g.
8: 67.2 l.
9: 33.6.
10: 12.5 g.
11: 8.4 l.
12: 750 g.
13: 3.04 g.
14: 26.35.
15: 0.2143 g.
16: 168 l.

Page 132
6: 122.5.
7: 98; 342.

Page 146
1: AsH_3.
2: C_2N_2.
3: $N_2H_4O_2$.
4: C_2H_6.
5: C_2H_4.
6: Al_2O_3.
7: $FeCl_3$.
8: Cu_2S.

Page 147
9: Hg_2O.
10: $CHCl_3$.

Page 153
1: HCl:H, 2.74%; Cl, 97.26%. $BaCl_2$:Ba,65.86%; Cl, 34.14%.

Page 153—*Cont.*
Na_2SO_4: Na, 32.39%; S, 22.54%; O, 45.07%. H_2SO_4: H, 2.04 %; S, 32.65%; O, 65.31%. C_2H_5OH: C, 42.17%; H, 13.04%;O,44.79%.
2: 25.52 g.
3: 6 l. N_2 and 12 l. NH_3.
4: 5.97 l.
5: 15.39 g.
6: 3.65 l.
7: 4.02 l. and the same volume of CO_2.
8: 62.94, 36.00, 51.22, 14.75.
9: 12.83 g.
10: 8.85 g.
11: 16 g. O_2 and 12.30 l. CO_2.

Page 233
7: 91.25 g. HCl and 146.25 g. salt.

Page 253
8: 56.25 g.

Page 534
1: 8.33 l.
2: 7.5 l.
3: H, 7.79%; C, 92.21%.
4: 36.46 g.
5: 80 l.
6: 1885.5 c.c.
7: 1979 c.c.
8: 3.65 l.
9: AsH_3.
10: 0.99 g.
11: 1.49 l.

Page 535
12: 4,024 c.c.
13: (a) CH; (b) C_2H_2.
14: 700 c.c.
15: 27 g.
16: 97.18 l.
17: H_2O, 47.12%; Na, 12.04%;B,11.52%; O, 29.32%.
18: 82.14 g.
19: C, 92.31%; H, 7.69%
20: 1400 lbs.
21: 5.34 l.

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INTERNATIONAL ATOMIC WEIGHTS

	Symbol	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26.97	Neodymium	Nd	60	144.27
Antimony	Sb	51	121.76	Neon	Ne	10	20.18
Argon	A	18	39.94	Neptunium	Np	93	239
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.92	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Plutonium	Pu	94	239
Carbon	C	6	12.01	Potassium	K	19	39.096
Cerium	Ce	58	140.13	Praseodymium	Pr	59	140.92
Cesium	Cs	55	132.91	Protactinium	Pa	91	231
Chlorine	Cl	17	35.46	Radium	Ra	88	226.05
Chromium	Cr	24	52.01	Radon	Rn	86	222
Cobalt	Co	27	58.01	Rhenium	Re	75	186.31
Columbium	Cb	41	92.91	Rhodium	Rh	45	102.91
Copper	Cu	29	63.57	Rubidium	Rb	37	85.48
Dysprosium	Dy	66	162.46	Ruthenium	Ru	44	101.7
Erbium	Er	68	167.20	Samarium	Sm	62	150.43
Europium	Eu	63	152.00	Scandium	Sc	21	45.10
Fluorine	F	9	19.00	Selenium	Se	34	78.96
Gadolinium	Gd	64	156.90	Silicon	Si	14	28.06
Gallium	Ga	31	69.72	Silver	Ag	47	107.880
Germanium	Ge	32	72.60	Sodium	Na	11	22.997
Gold	Au	79	197.20	Strontium	Sr	38	87.63
Hafnium	Hf	72	178.60	Sulphur	S	16	32.06
Helium	He	2	4.003	Tantalum	Ta	73	180.88
Holmium	Ho	67	164.94	Tellurium	Te	52	127.61
Hydrogen	H	1	1.008	Terbium	Tb	65	159.2
Indium	In	49	114.76	Thallium	Tl	81	204.39
Iodine	I	53	126.92	Thorium	Th	90	232.12
Iridium	Ir	77	193.10	Thulium	Tm	69	169.4
Iron	Fe	26	55.85	Tin	Sn	50	118.70
Krypton	Kr	36	83.7	Titanium	Ti	22	47.90
Lanthanum	La	57	138.92	Tungsten	W	74	183.92
Lead	Pb	82	207.21	Uranium	U	92	238.07
Lithium	Li	3	6.94	Vanadium	V	23	50.95
Lutecium	Lu	71	175.00	Xenon	Xe	54	131.3
Magnesium	Mg	12	24.32	Ytterbium	Yb	70	173.04
Manganese	Mn	25	54.93	Yttrium	Y	39	88.92
Mercury	Hg	80	200.61	Zinc	Zn	30	65.38
Molybdenum	Mo	42	96.00	Zirconium	Zr	40	91.22

740
x 600
444,000

THE PERIODIC TABLE OF THE ELEMENTS

(Atomic numbers are placed above the symbol for each element in heavy type and the atomic weight below. A dash indicates either an undiscovered element or one whose atomic weight is undetermined.)

Group		O	I		II		III		IV		V		VI		VII		VIII (Transition Elements)		
Oxide and Hydride			R_2O	RH	RO	RH_2	R_2O_3	RH_3	RO_2	RH_4	R_2O_5	RH_3	RO_3	RH_2	R_2O_7	RH			
Family			A	B	A	B	A	B	A	B	A	B	A	B	A	B			
Period	**Series**		**1** H 1.008																
I (Short)		**2** He 4.002	**3** Li 6.94			**4** Be 9.02		**5** B 10.82		**6** C 12.01		**7** N 14.0		**8** O 16.0		**9** F 19			
II (Short)		**10** Ne 20.18	**11** Na 23.0			**12** Mg 24.32		**13** Al 26.97		**14** Si 28.06		**15** P 30.98		**16** S 32.06		**17** Cl 35.46			
III (Long)	1	**18** A 39.94	**19** K 39.10		**20** Ca 40.08		**21** Sc 45.10		**22** Ti 47.90		**23** V 50.95		**24** Cr 52.01		**25** Mn 54.93		**26** Fe 55.85	**27** Co 58.94	**28** Ni 58.69
	2			**29** Cu 63.57		**30** Zn 65.38		**31** Ga 69.72		**32** Ge 72.6		**33** As 74.91		**34** Se 78.96		**35** Br 79.92			
IV (Long)	1	**36** Kr 83.7	**37** Rb 85.48		**38** Sr 87.63		**39** Y 88.92		**40** Zr 91.22		**41** Cb 92.91		**42** Mo 95.95		**43** Ma —		**44** Ru 101.7	**45** Rh 102.91	**46** Pd 106.7
	2			**47** Ag 107.88		**48** Cd 112.41		**49** In 114.8		**50** Sn 118.7		**51** Sb 121.76		**52** Te 127.61		**53** I 126.9			
V (Long)	1	**54** Xe 131.3	**55** Cs 132.91		**56** Ba 137.36		**57-71*** Rare Earths		**72** Hf 178.6		**73** Ta 180.88		**74** W 183.92		**75** Re 186.3		**76** Os 190.2	**77** Ir 193.1	**78** Pt 195.23
	2			**79** Au 197.2		**80** Hg 200.6		**81** Tl 204.4		**82** Pb 207.21		**83** Bi 209		**84** Po 210		**85** — —			
VI (Long)	1	**86** Rn 222	**87** — —		**88** Ra 226.05		**89** Ac 228		**90** Th 232.12		**91** Pa 231		**92** U 238.07						

***THE RARE EARTH ELEMENTS** (not classified)

57	**58**	**59**	**60**	**61**	**62**	**63**	**64**	**65**	**66**	**67**	**68**	**69**	**70**	**71**
La	Ce	Pr	Nd	Il	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
138.9	140.1	140.9	144.27	—	150.43	152	156.9	159.2	162.46	164.94	167.2	169.4	173.04	175

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